Scientific and Technical Report No. 13

Anaerobic Digestion Model No.1 (ADM1)

BY

IWA Task Group for Mathematical Modelling of Anaerobic Wastewater Processes

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Preface

The IWA Anaerobic Digestion Model No. 1 is the outcome of an intensive and fruitful collaboration between a number of international experts in anaerobic process analysis, modelling and simulation. The idea evolved over years and was first publicly floated at the 8th IAWQ Anaerobic Digestion Conference in Sendai, Japan, in 1997. Over the following two years, initial discussions and a survey of the IAWQ Specialist Group members were conducted. Following a workshop at the IAWQ Biennial Conference in Vancouver in 1998, a formal task group was established and endorsed by IAWQ. The rate of progress increased drastically in late 1999 when Damien Batstone was appointed by the University of Queensland to coordinate the work on the model development. The most productive period was a four-day workshop attended by the whole Task Group in February 2000 in Kastanienbaum, Switzerland, where the full model structure and much of the details were discussed intensively and decided upon. Subsequently, implementation and testing of the model structure was conducted and necessary modifications made. At the same time, the report was prepared jointly by the task group members. The work finally culminated in the presentation of the model at the 9th IWA Anaerobic Digestion Conference in Antwerpen, Belgium, in September 2001.

This model was keenly anticipated, given the major success achieved with the Activated Sludge Model series in previous years. The initial feedback after the workshop was very positive and it is hoped that this model will be accepted widely as a common platform for anaerobic process modelling and simulation. This should encourage a broad application of this tool in anaerobic process research, development, operation and optimisation. The ultimate goal is that the model will foster a much more widespread utilisation of anaerobic process technologies in the future – particularly given its great potential for providing sustainable waste and wastewater treatment, while reducing energy demand and greenhouse gas emissions.

However, this model should not be regarded as the only or the best way to describe anaerobic processes. It is merely a common platform from which simulation applications for a wide range of specific processes should be developed. We know that the model has a number of shortcomings and compromises; some have been specifically identified and are discussed in the form of boxed inserts in the report. Therefore, the model will not be ideally suited to each and every application. Indeed, we hope that over the coming years many specific applications and extensions of the model will be developed and published, to allow an increasingly broader utilisation of this helpful and powerful tool in process development and optimisation. The open structure and common nomenclature should encourage the fast and efficient development of specific add-ons as required.

The ADM1 does not describe all the mechanisms occurring in anaerobic degradation – and likely never will. However, the aim is a tool that allows predictions of sufficient accuracy to be useful in process development, operation and optimisation. Due to the varying demands in these fields, a different degree of model calibration and validation will be required in each case.

We hope that the anaerobic process community will fully embrace this new model as a useful tool in the application of anaerobic degradation processes worldwide. This model is not owned by the IWA Task Group, but should be shared by the whole industry, researchers and users alike.

Associate Professor Jurg Keller
and the IWA Task Group for Mathematical Modelling of Anaerobic Digestion Processes

Summary

This scientific and technical report presents the Anaerobic Digestion Model No. 1 (ADM1) as proposed by the IWA Task Group for Mathematical Modelling of Anaerobic Digestion Processes. This summary gives an outline of the report, and presents the consensus model.

The report is divided into five main sections (as well as introduction and conclusions). The core of the ADM1 is in Chapters 2, 3 and 4. Chapter 2 establishes nomenclature and units; Chapter 3 discusses biochemical reaction structure, and Chapter 4 discusses physico-chemical reaction structure. Chapters 5 and 6 support the ADM1 by providing information for its implementation in a continuous-flow stirred-tank reactor (CSTR) system, and suggested parameter values, respectively. Four appendixes provide additional information to that contained in the main report. Processes and mechanisms omitted, and consequent limitations of the ADM1, are included throughout the report in boxed inserts.

The ADM1 is a structured model with disintegration and hydrolysis, acidogenesis, acetogenesis and methanogenesis steps. An overview of the structure is shown in Figure 3.1, while the biochemical kinetic matrix in ASM1 format is shown in Tables 3.1 and 3.2. Extracellular solubilisation steps are divided into disintegration and hydrolysis, of which the first is a largely non-biological step and converts composite particulate substrate to inerts, particulate carbohydrates, protein and lipids. The second is enzymatic hydrolysis of particulate carbohydrates, proteins and lipids to monosaccharides, amino acids and long chain fatty acids (LCFA), respectively. Disintegration is mainly included to describe degradation of composite particulate material with lumped characteristics (such as primary or waste-activated sludge), while the hydrolysis steps are to describe well defined, relatively pure substrates (such as cellulose, starch and protein feeds). All disintegration and hydrolysis processes are represented by first order kinetics.

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Two separate groups of acidogens degrade monosaccharide and amino acids to mixed organic acids, hydrogen and carbon dioxide. The organic acids are subsequently converted to acetate, hydrogen and carbon dioxide by acetogenic groups that utilise LCFA, butyrate and valerate (one group for the two substrates), and propionate. The hydrogen produced by these organisms is consumed by a hydrogen-utilising methanogenic group, and the acetate by an aceticlastic methanogenic group. Substrate-based uptake Monod-type kinetics (slightly different from ASM Monod growth-based kinetics in ASM) are used as the basis for all intracellular biochemical reactions. Death of biomass is represented by first order kinetics, and dead biomass is maintained in the system as composite particulate material. Inhibition functions include pH (all groups), hydrogen (acetogenic groups) and free ammonia (aceticlastic methanogens). pH inhibition is implemented as one of two empirical equations, while hydrogen and free ammonia inhibition are represented by non-competitive functions. The other uptake-regulating functions are secondary Monod kinetics for inorganic nitrogen (ammonia and ammonium), to prevent growth when nitrogen is limited, and competitive uptake of butyrate and valerate by the single group that utilises these two organic acids.

Mechanisms included to describe physico-chemical processes are acid-base reactions (to calculate concentrations of hydrogen ions, free ammonia and carbon dioxide), and non-equilibria liquid–gas transfer. Solids precipitation is not included. Methods are given to implement equations describing acid-base equilibrium as an implicit algebraic equation set or a number of additional kinetic rate equations. As a differential and algebraic equation (DAE) set, there are 26 dynamic state concentration variables, 19 biochemical kinetic processes, 3 gas–liquid transfer kinetic processes and 8 implicit algebraic variables per liquid vessel. As a differential equation (DE) set, there are 32 dynamic state concentration variables and an additional 6 acid-base kinetic processes per vessel.

1

Introduction to the ADM1

1.1 THE IMPORTANCE OF ANAEROBIC DIGESTION AND A GENERIC PROCESS MODEL

Anaerobic conversions are among the oldest biological process technologies utilised by mankind, initially mainly for food and beverage production. They have been applied and developed over many centuries, although the most dramatic advances have been achieved in the last few decades with the introduction of various forms of high-rate treatment processes, particularly for industrial wastewater.

High organic loading rates and low sludge production are among the many advantages anaerobic processes exhibit over other biological unit operations. But the one feature emerging as a major driver for the increased application of anaerobic processes is the energy production. Not only does this technology have a positive net energy production but the biogas produced can also replace fossil fuel sources and therefore has a direct positive effect on greenhouse gas reduction. This will ensure the ongoing, and likely drastically increased, popularity of anaerobic digestion processes for waste treatment in the future.

But why is there a need for a generic model? Several benefits are expected from the production of this first generalised model of anaerobic digestion:

- increased model application for full-scale plant design, operation and optimisation;
- further development work on process optimisation and control, aimed at direct implementation in full-scale plants;
- common basis for further model development and validation studies to make outcomes more comparable and compatible;
- assisting technology transfer from research to industry.

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Many of the above points relate to practical, industrial applications. Indeed, this is one of the areas where most benefits from the application of a generic process model can be gained. While many different anaerobic models have been devised over the years (and indeed form the basis of the ADM1), their use by engineers, process technology providers and operators has been very limited. Two of the limiting factors have likely been the wide variety of models available and often their very specific nature.

The model presented in this report tries to be as widely applicable as possible for anaerobic processes – and therefore will naturally not be as accurate as some specific models developed for certain applications. And it also has been limited to the main relevant processes occurring in order to make it more simple and applicable. This again meant that many known and sometimes relevant aspects have not been included in this first version of the model. Some of these aspects are highlighted in this report in the form of boxed inserts, which briefly discuss the nature of the excluded process(es), and suggest conceptual approaches for extension of the ADM1.

We hope that this model will help to achieve a widespread utilisation of the large body of knowledge in anaerobic processes available from research studies and operational experience. This ultimately will support the increased application of anaerobic technology as one of the most sustainable waste treatment options in the future and a viable alternative to other energy generation processes.

1.2 CONVERSION PROCESSES IN ANAEROBIC DIGESTION

Conversion processes in anaerobic digestion can be divided into two main types (Figure 1.1):

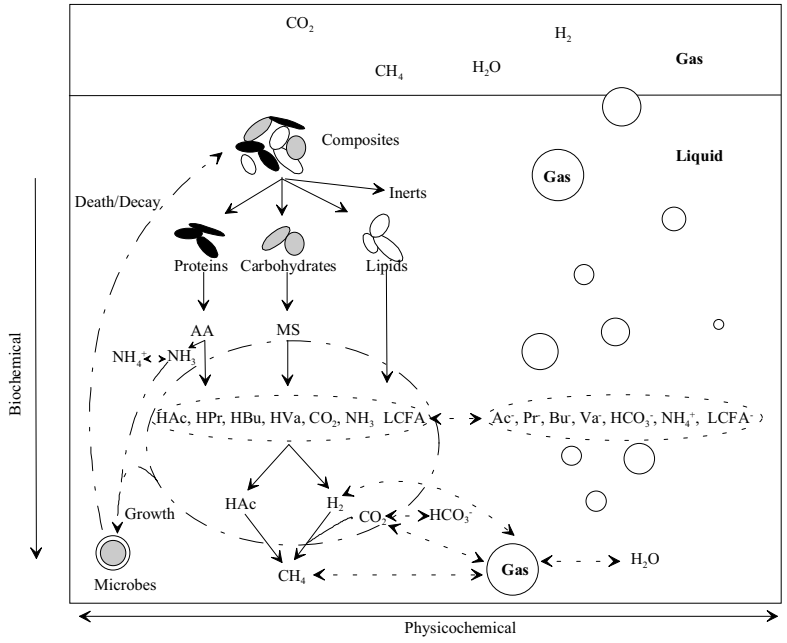

Figure 1.1: Conversion processes in anaerobic digestion as used in the model. Biochemical reactions are implemented as irreversible, while physico-chemical reactions are implemented as reversible. Abbreviations include MS (monosaccharides); AA (amino acids); LCFA (long chain fatty acids); LCFA$^-$ (LCFA base equivalent); HVa (valeric acid); Va$^-$ (valerate); HBu (butyric acid); Bu$^-$ (butyrate); HPr (propionic acid); Pr$^-$ (propionate); HAc (acetic acid); Ac$^-$ (acetate).

(1) Biochemical: These processes are normally catalysed by intra- or extracellular enzymes and act on the pool of available organic material. Disintegration of composites (such as dead biomass) to particulate constituents and their subsequent enzymatic hydrolysis to soluble monomers are extracellular processes. Digestion of soluble materials mediated by organisms is intracellular and this process results in biomass growth and decay.
(2) Physico-chemical: These processes are not biologically mediated and encompass ion association/dissociation, and gas–liquid transfer. Precipitation would be a further physico-chemical process; however, this is not included in the model.

Distinguishing between available degradable (substrate) and total input chemical oxygen demand (COD) is very important, as a considerable fraction of the input COD may be anaerobically not biodegradable (Gossett and Belser 1982). The ultimate biodegradability factor (D) is one of the most important characteristics of the influent COD, as it fundamentally influences all steps and COD flux. An influent with D = 1, or totally degradable organic components, is seldom found. In general, we use the term 'substrate' to indicate degradable COD, while the inert fraction (1 – D) is represented by the soluble (S_I) and particulate (X_I) inerts.

Biochemical equations are the core of any model and it is possible to represent an anaerobic system using only these equations. However, to describe the effect on biochemical reactions of the physico-chemical state (such as pH and gas concentrations) on biochemical reactions, physico-chemical conversions must be included as well.

The COD flow chart as used in this model is shown in Figure 1.2, which shows the COD flow through intermediates for a hypothetical composite particulate material that is 10% inerts, with the remainder split equally between carbohydrates, proteins and lipids. The COD flux would change considerably for different primary components, or for different product fractions from monosaccharide and amino acid acidogenesis.

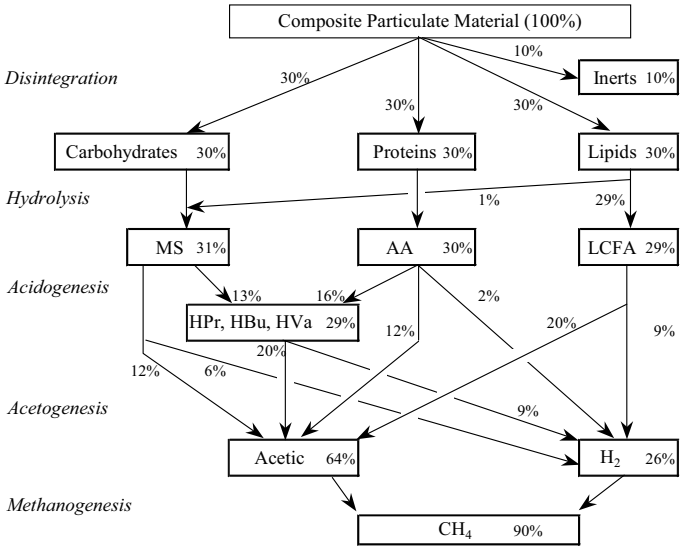

Figure 1.2: COD flux for a particulate composite comprised of 10% inerts, and 30% each of carbohydrates, proteins and lipids (in terms of COD). Propionic acid (10%), butyric acid (12%) and valeric acid (7%) are grouped in the figure for simplicity. Abbreviations are as for Figure 1.1.

2

Nomenclature, state variables and expressions

The IWA Anaerobic Digestion Model No. 1 (ADM1) introduces generic nomenclature, units and definitions. This chapter presents these, and serves as a reference for terms used throughout the report. The empirical formula of $C_5H_7O_2N$ is used to represent biomass as in the ASM series (Henze *et al.* 1987).

2.1 UNITS

The units to be used were the subject of extensive discussion and a community survey. COD (kgCOD $m^{-3} \equiv$ gCOD m^{-1}) was chosen as the chemical component base unit because of its use as a wastewater characterisation measure in concentrated streams, its use in upstream and gas utilisation industries, the implicit balancing of carbon oxidation state and to enable partial compatibility with the IWA Activated Sludge Models (Henze *et al.* 1987). Molar basis (kmole $m^{-3} \equiv$ M) is used for components with no COD such as inorganic carbon (CO_2 and HCO_3^-) and inorganic nitrogen (NH_4^+ and NH_3).

A molar (M) and kgCOD m^{-3} basis was chosen to facilitate $\log_{10}$ conversions (e.g. pH and pK_a) for physico-chemical equations. The use of kgCOD m^{-3} is not in agreement with the Activated Sludge Models and general practice in aerobic treatment, where gCOD m^{-3} (mgCOD l^{-1}) is commonly used. However, implementing in mgCOD l^{-1} is relatively simple, as it requires only changes in K_S values, and modification of pK_a and K_a values, and we encourage the use of gCOD m^{-3} (mgCOD l^{-1}) if required (e.g. as an add-in to aerobic models). Use of the model in gCOD m^{-3} (mgCOD l^{-1}) and integration with the ASM models is specifically addressed in Appendix C.

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Table 2.1: Units.

Measure	Units
concentration	kgCOD m^{-3}
Concentration (non-COD)	kmoleC m^{-3}
Concentration (nitrogen non-COD)	kmoleN m^{-3}
Pressure	bar
Temperature	K
Distance	m
Volume	m^3
Energy	J (kJ)
Time	d (day)

2.2 NOMENCLATURE AND DESCRIPTION OF PARAMETERS AND VARIABLES

There are four main types of parameters and variables: stoichiometric coefficients, equilibrium coefficients, kinetic parameters, and dynamic state and algebraic variables.

Table 2.2: Stoichiometric coefficients.

Symbol	Description	Units
C_i	Carbon content of component i	kmoleC $kgCOD^{-1}$
N_i	Nitrogen content of component i	kmoleN $kgCOD^{-1}$
$\nu_{i,j}$	Rate coefficients for component i on process j	nominally kgCOD m^{-3}
$f_{product,substrate}$	Yield (catabolism only) of product on substrate	kgCOD $kgCOD^{-1}$

Table 2.3: Equilibrium coefficients and constants.

Symbol	Description	Units
H_{gas}	Gas law constant (equal to K_H^{-1})	bar M^{-1} (bar m^3 $kmole^{-1}$)
$K_{a,acid}$	Acid-base equilibrium coefficient	M (kmole m^{-3})
K_H	Henry's law coefficient	M bar^{-1} (kmole m^{-3} bar^{-1})
pK_a	$-\log_{10}[K_a]$	
R[1]	Gas law constant (8.314×10^{-2})	bar M^{-1} K^{-1} (bar m^3 $kmole^{-1}$ K^{-1})
ΔG	Free energy	J. $mole^{-1}$

[1] A value of R equal to 8.314 J $mole^{-1}$ K^{-1} should be used in the van't Hoff equation (Eq. (4.10)) for consistency of units.

Table 2.4: Kinetic parameters and rates.

Symbol	Description	Units
$k_{A/Bi}$	Acid base kinetic parameter	$M^{-1}d^{-1}$
k_{dec}	First order decay rate	d^{-1}
$I_{inhibitor,\ process}$	Inhibition function (see K_I)	
$k_{process}$	First order parameter (normally for hydrolysis)	d^{-1}
k_La	Gas–liquid transfer coefficient	d^{-1}
$K_{I,\ inhibit,\ substrate}$	50% inhibitory concentration	kgCOD m^{-3}
$k_{m,\ process}$	Monod maximum specific uptake rate (μ_{max}/Y)	kgCOD_S $kgCOD\_X^{-1}$ d^{-1}
$K_{S,process}$	Half saturation value	kgCOD_S m^{-3}
ρ_j	Kinetic rate of process j	kgCOD_S m^{-3} d^{-1}
$Y_{substrate}$	Yield of biomass on substrate	kgCOD_X $kgCOD\_S^{-1}$
μ_{max}	Monod maximum specific growth rate	d^{-1}

Table 2.5: Dynamic state and algebraic variables (and derived variables).

Symbol	Description	Units
pH	$-\log_{10}[H^+]$	
$p_{gas,i}$	Pressure of gas i	bar
P_{gas}	Total gas pressure	bar
S_i	Soluble component i	kgCOD m^{-3}
$t_{res,X}$	Extended retention of solids	d
T	Temperature	K
V	Volume	m^3
X_i	Particulate component i	kgCOD m^{-3}

2.3 DYNAMIC STATE VARIABLES

This section lists the dynamic state variables as used in the ADM1 in a differential and algebraic equation (DAE) implementation (Chapter 5). Dynamic state variables are those calculated at a specified time (t) by solution of the set of differential equations as defined by the ADM1 process rates, the process configuration modelled, inputs, and the initial conditions (i.e. the values of these states at t = 0). As such, when a DAE implementation is used, the state of a system at time = t is fully defined by the value of these 26 variables in each vessel. Because of the fast dynamics of acid-base reactions, this is also effectively true when using a differential equation (DE) implementation although there are 32 dynamic state variables.

Table 2.6: Dynamic state variable characteristics (DAE system).

Name	i[1]	Description	Units[2]	MW	gCOD·mole^{-1}	Carbon content (C_i)	Nitrogen Content (N_i)
X_c	13	composite		varies	varies	varies	varies
X_{ch}	14	carbohydrates		varies	varies	0.0313	0
X_{pr}	15	proteins[3]		varies	varies	varies	varies
X_{li}	16	lipids[4]		806	2320	0.0220	0
X_I	24	particulate inerts		varies	varies	varies	varies
S_I	12	soluble inerts		varies	varies	varies	varies
S_{su}	1	monosaccharides		180	192	0.0313	0
S_{aa}	2	amino acids[3]		varies	varies	varies	varies
S_{fa}	3	total LCFA[4]		256	736	0.0217	0
S_{va}	4	total valerate		102	208	0.0240	0
S_{bu}	5	total butyrate		88	160	0.0250	0
S_{pro}	6	total propionate		74	112	0.0268	0
S_{ac}	7	total acetate		60	64	0.0313	0
S_{h2}	8	hydrogen		2	16	0	0
S_{ch4}	9	methane		16	64	0.0156	0
S_{IC}	10	inorganic carbon	M	44	0	1	0
S_{IN}	11	inorganic nitrogen	M	17	0	0	1
X_{su-h2}	17-23	biomass		113	160	0.0313	0.00625
S_{cat}		cations	M	varies	0	0	0
S_{an}		anions	M	varies	0	0	0

1. See process kinetics and stoichiometry matrix in Tables 3.1 and 3.2.
2. Unless otherwise stated, kgCOD m^{-3}.
3. See Appendix D.
4. Based on palmitic triglyceride as lipid and palmitate as LCFA.

3

Biochemical processes

3.1 STRUCTURE OF BIOCHEMICAL REACTIONS IN THE ADM1

Most recent anaerobic digestion models include intermediate products, and the task group agreed on a structured model because of a number of scientific and application advantages. The philosophy of process and component inclusion was to maximise applicability while maintaining a reasonably simple structure. Reasons for including specific processes are explained under sub-headings. The model includes the three overall biochemical (cellular) steps (acidogenesis [fermentation], acetogenesis [anaerobic oxidation of organic acids] and methanogenesis) as well as an extracellular (partly non-biological) disintegration step and an extracellular hydrolysis step (Figure 3.1). Three of the processes (hydrolysis, acidogenesis and acetogenesis) have a number of parallel reactions.

Complex composite particulate waste is assumed to be homogeneous, which disintegrates to carbohydrate, protein and lipid particulate substrate. This was mainly included to facilitate modelling of waste activated sludge digestion, as a disintegration step is thought to precede more complex hydrolytic steps (Pavlostathis and Gossett 1988), but is also generally used when the primary substrate can be represented with lumped kinetic and biodegradability parameters (e.g. primary sludge and other substrates; see Appendix A). The complex particulate pool is also used as a pre-lysis repository of dead biomass. Therefore the disintegration step is intended to include an array of steps such as lysis, non-enzymatic decay, phase separation and physical breakdown (e.g. shearing).

All extracellular steps were assumed to be first order, which is an empirical function reflecting the cumulative effect of a multi-step process (Eastman and Ferguson 1981). Cellular kinetics are described by three expressions (uptake, growth, decay; see Tables 3.1 and 3.2).

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Table 3.1: Biochemical rate coefficients ($\nu_{i,j}$) and kinetic rate equations (ρ_j) for soluble components (i = 1–12; j = 1–19).

	Component → i	1	2	3	4	5	6	7	8	9	10	11	12	
j	Process ↓	S_{su}	S_{aa}	S_{fa}	S_{va}	S_{bu}	S_{pro}	S_{ac}	S_{h2}	S_{ch4}	S_{IC}	S_{IN}	S_I	Rate (ρ_j, kg COD.m^{-3}.d^{-1})
1	Disintegration												$f_{sI,xc}$	$k_{dis}X_c$
2	Hydrolysis Carbohydrates	1												$k_{hyd,ch}X_{ch}$
3	Hydrolysis of Proteins		1											$k_{hyd,pr}X_{pr}$
4	Hydrolysis of Lipids	$1-f_{fa,li}$		$f_{fa,li}$										$k_{hyd,li}X_{li}$
5	Uptake of Sugars	-1				$(1-Y_{su})\,f_{bu,su}$	$(1-Y_{su})\,f_{pro,su}$	$(1-Y_{su})\,f_{ac,su}$	$(1-Y_{su})\,f_{h2,su}$		$-\sum_{i=1-9,11-24} C_i\nu_{i,5}$	$-(Y_{su})\,N_{bac}$		$k_{m,su}\frac{S_{su}}{K_S+S}X_{su}I_1$
6	Uptake of Amino Acids		-1		$(1-Y_{aa})\,f_{va,aa}$	$(1-Y_{aa})\,f_{bu,aa}$	$(1-Y_{aa})\,f_{pro,aa}$	$(1-Y_{aa})\,f_{ac,aa}$	$(1-Y_{aa})\,f_{h2,aa}$		$-\sum_{i=1-9,11-24} C_i\nu_{i,6}$	$N_{aa}-(Y_{aa})\,N_{bac}$		$k_{m,aa}\frac{S_{aa}}{K_S+S_{aa}}X_{aa}I_1$
7	Uptake of LCFA			-1				$(1-Y_{fa})\,0.7$	$(1-Y_{fa})\,0.3$			$-(Y_{fa})\,N_{bac}$		$k_{m,fa}\frac{S_{fa}}{K_S+S_{fa}}X_{fa}I_2$
8	Uptake of Valerate				-1		$(1-Y_{c4})\,0.54$	$(1-Y_{c4})\,0.31$	$(1-Y_{c4})\,0.15$			$-(Y_{c4})\,N_{bac}$		$k_{m,c4}\frac{S_{va}}{K_S+S_{va}}X_{c4}\frac{1}{1+S_{bu}/S_{va}}I_2$
9	Uptake of Butyrate					-1		$(1-Y_{c4})\,0.8$	$(1-Y_{c4})\,0.2$			$-(Y_{c4})\,N_{bac}$		$k_{m,c4}\frac{S_{bu}}{K_S+S_{bu}}X_{c4}\frac{1}{1+S_{va}/S_{bu}}I_2$
10	Uptake of Propionate						-1	$(1-Y_{pro})\,0.57$	$(1-Y_{pro})\,0.43$		$-\sum_{i=1\ 9,11\ 24} C_i\nu_{i,10}$	$-(Y_{pro})\,N_{bac}$		$k_{m,pr}\frac{S_{pro}}{K_S+S_{pro}}X_{pro}I_2$
11	Uptake of Acetate							-1		$(1-Y_{ac})$	$-\sum_{i=1-9,11-24} C_i\nu_{i,11}$	$-(Y_{ac})\,N_{bac}$		$k_{m,ac}\frac{S_{ac}}{K_S+S_{ac}}X_{ac}I_3$
12	Uptake of Hydrogen								-1	$(1-Y_{h2})$	$-\sum_{i=1-9,11-24} C_i\nu_{i,12}$	$-(Y_{h2})\,N_{bac}$		$k_{m,h2}\frac{S_{h2}}{K_S+S_{h2}}X_{h2}I_1$
13	Decay of X_{su}													$k_{dec,Xsu}X_{su}$
14	Decay of X_{aa}													$k_{dec,Xaa}X_{aa}$
15	Decay of X_{fa}													$k_{dec,Xfa}X_{fa}$
16	Decay of X_{C4}													$k_{dec,Xc4}X_{c4}$
17	Decay of X_{pro}													$k_{dec,Xpro}X_{pro}$
18	Decay of X_{ac}													$k_{dec,Xac}X_{ac}$
19	Decay of X_{h2}													$k_{dec,Xh2}X_{h2}$
		Monosaccharides (kgCOD m^{-3})	Amino Acids (kgCOD m^{-3})	Long chain fatty acids (kgCOD m^{-3})	Total valerate (kgCOD m^{-3})	Total butyrate (kgCOD m^{-3})	Total propionate (kgCOD m^{-3})	Total acetate (kgCOD m^{-3})	Hydrogen gas (kgCOD m^{-3})	Methane gas (kgCOD m^{-3})	Inorganic Carbon (kmoleC m^{-3})	Inorganic nitrogen (kmoleN m^{-3})	Soluble inerts (kgCOD m^{-3})	Inhibition factors (3.7): $I_1 = I_{pH}I_{IN,lim}$ $I_2 = I_{pH}I_{IN,lim}I_{h2}$ $I_3 = I_{pH}I_{IN,lim}I_{NH3,Xac}$

Table 3.2: Biochemical rate coefficients ($\nu_{i,j}$) and kinetic rate equations (ρ_j) for particulate components (i = 13–24; j = 1–19).

Component → i		13	14	15	16	17	18	19	20	21	22	23	24	Rate (ρ_j, kg COD.m^{-3}.d^{-1})
j	Process ↓	X_c	X_{ch}	X_{pr}	X_{li}	X_{su}	X_{aa}	X_{fa}	X_{c4}	X_{pro}	X_{ac}	X_{h2}	X_I	
1	Disintegration	-1	$f_{ch,xc}$	$f_{pr,xc}$	$f_{li,xc}$								$f_{xI,xc}$	$k_{dis}X_c$
2	Hydrolysis Carbohydrates		-1											$k_{hyd,ch}X_{ch}$
3	Hydrolysis of Proteins			-1										$k_{hyd,pr}X_{pr}$
4	Hydrolysis of Lipids				-1									$k_{hyd,li}X_{li}$
5	Uptake of Sugars					Y_{su}								$k_{m,su}\frac{S_{su}}{K_S+S}X_{su}I_1$
6	Uptake of Amino Acids						Y_{aa}							$k_{m,aa}\frac{S_{aa}}{K_S+S_{aa}}X_{aa}I_1$
7	Uptake of LCFA							Y_{fa}						$k_{m,fa}\frac{S_{fa}}{K_S+S_{fa}}X_{fa}I_2$
8	Uptake of Valerate								Y_{c4}					$k_{m,c4}\frac{S_{va}}{K_S+S_{va}}X_{c4}\frac{1}{1+S_{bu}/S_{va}}I_2$
9	Uptake of Butyrate								Y_{c4}					$k_{m,c4}\frac{S_{bu}}{K_S+S_{bu}}X_{c4}\frac{1}{1+S_{va}/S_{bu}}I_2$
10	Uptake of Propionate									Y_{pro}				$k_{m,pr}\frac{S_{pro}}{K_S+S_{pro}}X_{pro}I_2$
11	Uptake of Acetate										Y_{ac}			$k_{m,ac}\frac{S_{ac}}{K_S+S_{ac}}X_{ac}I_3$
12	Uptake of Hydrogen											Y_{h2}		$k_{m,h2}\frac{S_{h2}}{K_S+S_{h2}}X_{h2}I_1$
13	Decay of X_{su}	1				-1								$k_{dec,Xsu}X_{su}$
14	Decay of X_{aa}	1					-1							$k_{dec,Xaa}X_{aa}$
15	Decay of X_{fa}	1						-1						$k_{dec,Xfa}X_{fa}$
16	Decay of X_{c4}	1							-1					$k_{dec,Xc4}X_{c4}$
17	Decay of X_{pro}	1								-1				$k_{dec,Xpro}X_{pro}$
18	Decay of X_{ac}	1									-1			$k_{dec,Xac}X_{ac}$
19	Decay of X_{h2}	1										-1		$k_{dec,Xh2}X_{h2}$
		Composites (kgCOD m^{-3})	Carbohydrates (kgCOD m^{-3})	Proteins (kgCOD m^{-3})	Lipids (kgCOD m^{-3})	Sugar degraders (kgCOD m^{-3})	Amino acid degraders (kgCOD m^{-3})	LCFA degraders (kgCOD m^{-3})	Valerate and butyrate degraders (kgCOD m^{-3})	Propionate degraders (kgCOD m^{-3})	Acetate degraders (kgCOD m^{-3})	Hydrogen degraders (kgCOD m^{-3})	Particulate inerts (kgCOD m^{-3})	Inhibition factors (3.7): $I_1 = I_{pH}I_{IN,lim}$ $I_2 = I_{pH}I_{IN,lim}I_{h_2}$ $I_3 = I_{pH}I_{IN,lim}I_{NH3,Xac}$

The key rate equation is substrate uptake, which is based on substrate level Monod-type kinetics. We chose substrate uptake related kinetics (rather than growth related kinetics) to decouple growth from uptake, and allow variable yields. More reasons for this are given in Section 3.7 on inhibition, and practical differences are addressed in Appendix C. The basic kinetics used here could also be termed Michaelis–Menten, but this is not a term generally used for autocatalysis, and as Speece (1996) did, we use the term Monod-type. Biomass growth is implicit in substrate uptake. First order biomass decay (to composite particulate material) was assumed and is described with an independent set of expressions.

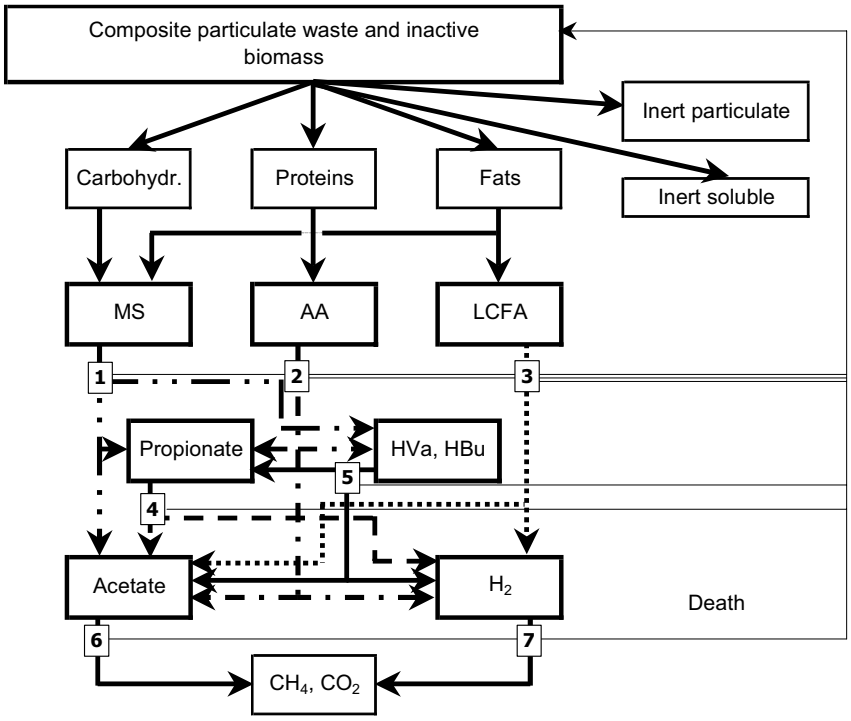

Figure 3.1: The anaerobic model as implemented including biochemical processes (1) acidogenesis from sugars; (2) acidogenesis from amino acids; (3) acetogenesis from LCFA; (4) acetogenesis from propionate; (5) acetogenesis from butyrate and valerate; (6) aceticlastic methanogenesis; and (7) hydrogenotrophic methanogenesis.

3.2 RATE EQUATION MATRIX

The process rate and stoichiometry matrix for biochemical reactions are given in Tables 3.1 (soluble components) and 3.2 (particulate components) in the same format as the ASM series. Physico-chemical rate equations (such as liquid–gas transfer) are not included in these tables. An explanation of this form of rate presentation and physico-chemical portions of the matrix is given in Appendix B. All acid-base pairs, including organic acids, are represented as the sum of the acid/base pair concentrations (e.g. $S_{IC} = S_{CO2} + S_{HCO3}$ and $S_{ac} = S_{Ac-} + S_{HAc}$). More information about modelling of the physico-chemical equations, and the option of splitting these pairs as dynamic state variables, is given in Chapter 4. Where fitted or

calculated products on substrate yields are used, they are referred to as $f_{\text{product, substrate}}$. COD balancing is implicit in the matrix. In many cases, inorganic carbon is the carbon source for, or a product of, catabolism or anabolism (i.e. uptake of sugars, amino acids, propionate, acetate and hydrogen; j = 5,6,10,11,12) and, in these cases, we recommend expressing the inorganic carbon rate coefficient as a carbon balance:

$$\nu_{10,j} = -\sum_{i=1-9,11-24} C_i \nu_{i,j} \tag{3.1}$$

For example, $\nu_{10,6}$, the inorganic carbon coefficient for amino acid fermentation, is:

$$\begin{aligned}\nu_{10,6} = -(-C_{aa} + (1 - Y_{aa}) f_{va,aa,\,Cva} + (1 - Y_{aa}) f_{bu,aa} C_{bu} + (1 - Y_{aa}) f_{pro,aa} C_{pro} \\ + (1 - Y_{aa}) f_{ac,aa} C_{ac} + Y_{aa} C_{biom})\end{aligned} \tag{3.2}$$

where C_i is the carbon content (kgmoleC kgCOD^{-1}) of component i, and C_{biom} is the general carbon content of biomass (0.0313 moleC gCOD^{-1}). In other processes, (disintegration, hydrolysis, uptake of LCFA, valerate, butyrate, decay: j = 1 – 4,7,8,9,13–19), we decided not to include this term. There may be a small error in the carbon balances of these processes because of the different carbon contents of substrate, product and biomass. If necessary, to avoid this error in the carbon balance, Eq. (3.1) can be used as the stoichiometric coefficient $\nu_{10,j}$ for all biochemical processes (i.e. j = 1 – 24).

3.3 DISINTEGRATION AND HYDROLYSIS

Disintegration and hydrolysis are extracellular biological and non-biological processes mediating the breakdown and solubilisation of complex organic material to soluble substrates. The substrates are complex composite particulates and particulate carbohydrates, proteins and lipids. The last three substrates are also products from disintegration of composite particulates. Other products of disintegration are inert particulate and inert soluble material. The products from (enzymatic) degradation of carbohydrates, proteins and lipids are monosaccharides, amino acids and long chain fatty acids, respectively.

A mainly non-biological disintegration step was included as the first process to allow diversity of application, and to allow for lysis of biological sludge and complex organic material. The three parallel enzymatic steps were included to account for the difference in hydrolysis rates of the three well-defined particulate substrates.

The disintegration step was also included to represent the pool of composite organic material. This is especially important for waste-activated and primary sludge digestion, where the disintegration step represents lysis of whole cells and separation of composites. Vavilin and co-workers (e.g. Vavilin *et al.* 1999), Pavlostathis and Gossett (1988) and O'Rourke (1968) have used this approach. Inclusion of a composite organic material also allows an elegant method for recycling of dead anaerobic biomass.

The term hydrolysis is used here to mean the degradation of a defined particulate or macromolecular substrate to its soluble monomers. The most significant particulate substrates identified were carbohydrates, proteins and lipids, and for these substrates, the depolymerisation process matches the formal chemical definition of hydrolysis. In each case, the process is catalysed by enzymes, which are likely produced by the organism directly benefiting from the soluble products.

Hydrolysis can be represented by one of two conceptual models:

(1) The organisms secrete enzymes to the bulk liquid where they adsorb onto a particle or react with a soluble substrate.
(2) The organisms attach to a particle, produce enzymes in the vicinity of the particle and benefit from soluble products released by the enzymatic reaction.

The task group agreed that in anaerobic mixed culture systems the dominant mechanisms found were of type (2) as shown by Vavilin *et al*. (1996) and Sanders *et al.* (2000). Therefore, the organisms growing on the particle surface, rather than the enzyme produced, should be regarded as the effective catalyst.

3.3.1 Kinetics of disintegration and hydrolysis

All literature models utilising a disintegration term (as opposed to a hydrolysis term) have used first order kinetics. This is reasonable, as first order kinetics have been supported by observations, and because the diversity of disintegration processes cannot support a different, more fundamental approach in a generic model.

The complete enzymatic hydrolysis step is a complex multi-step process for carbohydrates, proteins and lipids, which may include multiple enzyme production, diffusion, adsorption, reaction and enzyme deactivation steps. However, the most commonly used kinetic relationship to describe hydrolysis processes is first order and 'is an empirical expression that reflects the cumulative effect of all the microscopic processes occurring…' (Eastman and Ferguson 1981). Surface-related hydrolysis kinetics have been based on enzyme production or adsorption (Batstone *et al.* 2000; Jain *et al.* 1992), or surface-related biomass growth (Vavilin *et al.* 1996). Walker and Wilson (1991), Negri *et al*. (1993) and Sanders *et al.* (2000) have used models to demonstrate the importance of surface-based kinetics more empirically.

However, Vavilin *et al.* (1996) compared a number of hydrolysis kinetics including a two-phase surface-related model. A first order model was only slightly poorer than the more complex two-phase model. A model with Contois kinetics (which use a single parameter to represent saturation of both substrate and biomass) was as good at fitting the data as the two-phase model. Valentini *et al*. (1997) quantitatively assessed the influence of biomass concentration in a first order model, with an exponent of between 0 and 1 affecting the biomass concentration, finding that the exponent had a best fit between 0.4 and 0.6 (batch tests). An exponent of 0 (i.e. biomass-independent, first-order substrate-based) was almost as effective as the optimal exponent with a standard deviation of 35% compared to an optimum of 22%. Batstone (2000) also showed that a first order model could fit biogas production as well as a complex two-phase model (which included enzyme adsorption). Therefore the task group recommends that first order kinetics be used by default. Contois kinetics could be used in systems where biomass to substrate ratios are low enough to be rate-limiting (e.g. in batch digestion; see Vavilin *et al.* (1996) for equations).

3.4 MIXED PRODUCT ACIDOGENESIS

Acidogenesis (fermentation) is generally defined as an anaerobic acid-producing microbial process without an additional electron acceptor or donor (Gujer and Zehnder 1983). This includes the degradation of soluble sugars and amino acids to a number of simpler products. The degradation of LCFA is an oxidation reaction with an external electron acceptor and is

therefore included in Section 3.5 on acetogenesis. Because acidogenesis (as opposed to acetogenesis) can occur without an additional electron acceptor, and because free energy yields are normally higher, the reactions can occur at high hydrogen or formate concentrations and at higher biomass yields.

3.4.1 Acidogenesis from monosaccharides

The task group decided to use glucose (hexoses) as the model monomer. Fructose is energetically and stoichiometrically equivalent for modelling purposes, and pentoses will have similar stoichiometric yields compared to hexoses, with one less CO_2 or carboxylic acid unit in the products. The most important products and their stoichiometric reaction from glucose with approximate ATP yields are ranked in order of importance in Table 3.3. These acids can also be produced in combination for mixed acid products.

Table 3.3: Products from glucose degradation.

	Products	Reaction	ATP per mole glucose	Conditions	Note
(i)	Acetate	$C_6H_{12}O_6+2H_2O \rightarrow 2CH_3COOH+2CO_2+4H_2$	4	low H_2	1
(ii)	Propionate	$C_6H_{12}O_6+2H_2 \rightarrow 2CH_3CH_2COOH+2H_2O$	~low	not observed	2
(ii')	Acetate, Propionate	$3C_6H_{12}O_6 \rightarrow 4CH_3CH_2COOH+2CH_3COOH+2CO_2+2H_2O$	4/3	any H_2	
(iii)	Butyrate	$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH+2CO_2+2H_2$	3	low H_2	1
(iv)	Lactate	$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$	2	any H_2	
(v)	Ethanol	$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH+2CO_2$	2	low pH	3

1. While thermodynamically possible at high H_2, may be limited by energetics of substrate-level phosphorylation (Schink 2001).
2. Not yet observed in cultured environmental samples. Coupling with substrate level oxidation is more common as in reaction ii'.
3. Energy yield taken from yeast pathway. Bacterial pathway may have 0 ATP/mole ethanol (Madigan *et al.* 2000).

Reaction (ii), which is the uncoupled reaction of glucose to propionate, has appeared in several models (Costello *et al* 1991; Romli *et al.* 1995; Skiadas *et al.* 2000). However, the task group recommends that reaction (ii') be used in preference to reaction (ii) for the following reasons:

(1) No organism producing propionate only has been cultured. All organisms producing propionate or succinate (the key intermediate prior to propionate) also produce acetate with CO_2 as by-product (Madigan *et al.* 2000; Gottschalk 1986).
(2) Sourcing electrons from (i.e. oxidising) formate or elemental hydrogen is thermodynamically unfavourable except at a high H_2 partial pressure and is therefore inconsistent with the release of formate or hydrogen by organisms fermenting monosaccharides to butyrate or acetate.

The task group decided to include acetate, propionate and butyrate in the model as they are important end-products from monosaccharide acidogenesis, are degraded differently downstream, and are measured simultaneously by gas chromatography (GC) analysis. Lactate and ethanol were not included in the ADM1 (see box).

ALTERNATIVE PRODUCTS FROM ACIDOGENESIS OF SUGARS

Glucose fermentation can result in a number of alternative fermentation products apart from organic acids (Madigan *et al.* 2000), the most important of which (in anaerobic digesters) are lactate and ethanol. Lactate is a key intermediate, and work has indicated that most or all of the monosaccharide substrate may degrade via lactate (Skiadas *et al.* 2000; Romli *et al.* 1995). However, lactate is subsequently degraded very quickly and is therefore seen primarily during transient overload conditions in acidification reactors. As seen in Romli *et al*. (1995), during the concentration overload, the lactate increases from being insignificant to the highest organic acid (in terms of COD). Ethanol is produced as an alternative to acetate at low pH (pH < 5.0; Ren *et al.* 1997).

Lactate has the same stoichiometry as glucose and, therefore, the biological reaction stoichiometry is not affected by its omission from the ADM1. However, lactic acid has a relatively low pK_a (3.08), which has a strong effect on pH values. In particular, the ADM1 will underpredict transient decreases in pH (i.e. overpredict pH during rapid dynamics). This effect is more pronounced for hydraulic increases as compared to concentration increases. The lack of ethanol as an intermediate will cause poor prediction of intermediate organic acids, and pH at low pH levels in acidification reactors. Methanogenic reactors and low-loaded systems will be largely unaffected by the omission of either lactate or ethanol, as lactate and ethanol are relatively easily degraded to mixed organic acids and acetate, respectively. The relatively low concentrations of these intermediates in most anaerobic digesters was the main reason for their omission from the ADM1. In general, it would be desirable to include them in highly loaded acidogenic glucose-fed systems, with transient concentration and hydraulic conditions (lactate), or when operated at low pH, or deliberately to promote ethanol production, for example to enhance downstream digestion (Ren *et al.* 1997).

Lactate has been implemented as an intermediate by Costello *et al.* (1991), Romli *et al*. (1995), and Skiadas *et al*. (2000). The simplest method is similar to the last, and assumes that all glucose degrades via lactate, which is subsequently degraded to mixed organic acids by either glucose degrading bacteria or by a dedicated group. References to models including degradation of glucose to ethanol have not been found and a regulation function is probably necessary to describe the dependence of product yields on pH.

Since many organisms are capable of producing several products, a single group of organisms with lumped parameters should be used. Regulation functions to describe the various fractions of products from monosaccharides under different H_2 and pH levels have been described by Mosey (1983) and further developed by Costello *et al.* (1991) and Romli *et al.* (1995). However, these are described using reactions (ii) and (iv), could not be used consistently with a variety of experimental data sets, and require the inclusion of lactate. Therefore, no hydrogen regulation function is used in the ADM1, and stoichiometric yields ($f_{h2,su}$, $f_{ac,su}$, $f_{pro,su}$, $f_{bu,su}$) should be set to values consistent with the equations in Table 3.3 (see Appendix D). Fixed stoichiometric yields were used by Skiadas *et al.* (2000) and Angelidaki *et al.* (1999).

3.4.2 Acidogenesis from amino acids

There are 20 common amino acids (see Appendix D). The relative yields of amino acids produced from the hydrolysis of protein are dependent on the protein primary structure (FAO, UN 1970). There are two main pathways for amino acid fermentation:

(1) Stickland oxidation-reduction paired fermentation.
(2) Oxidation of a single amino acid with hydrogen ions or carbon dioxide as the external electron acceptor.

Stickland reactions occur more rapidly than uncoupled degradation (Barker 1981) and in normal mixed-protein systems, there is normally only a 10% shortfall in electron acceptor proteins (Nagase and Matsuo 1982). There are a number of characteristics of Stickland fermentation of amino acids (Figure 3.2):

(1) Different amino acids can act as donors, acceptors, or both (Appendix D).
(2) The electron donor loses one carbon atom to CO_2 and forms a carboxylic acid with one carbon shorter than the original amino acid (i.e. alanine; C3 → acetate; C2).
(3) The electron acceptor retains carbon atoms to form a carboxylic acid with the same chain length as the original amino acid (i.e. glycine, C2 → acetate, C2).
(4) Only histidine cannot be degraded via Stickland reactions.
(5) Typically around 10% of total amino acids are degraded by uncoupled oxidation because of a shortfall in electron acceptors, and this results in hydrogen or formate production.

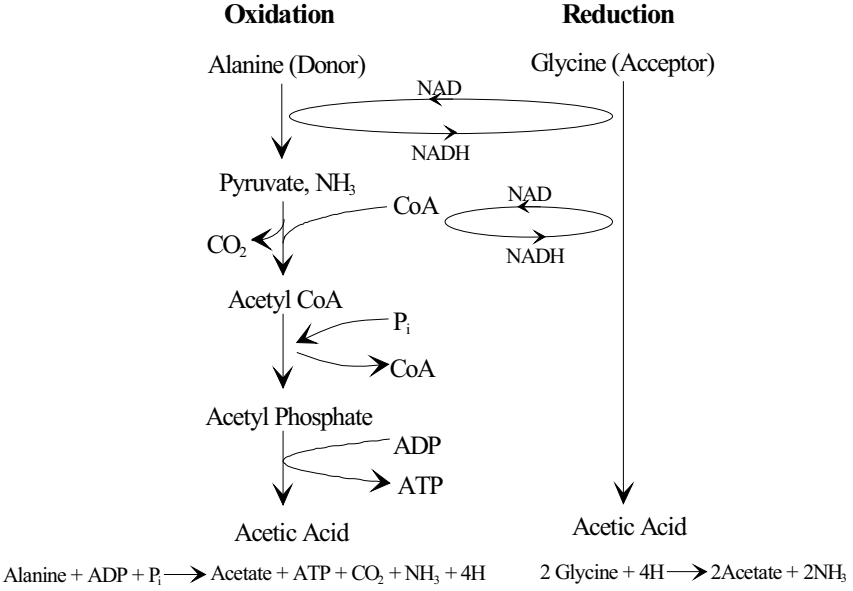

Figure 3.2: Coupled Stickland digestion of alanine and glycine (from Madigan *et al*. 2000).

This is important for modelling amino acid acidogenesis since, given the amino acid mixture of the source protein, the stoichiometric yields of products can be predicted. These are largely C2, C3, C4, C5, C6 iso and normal organic acids with some aromatics, CO_2, H_2, NH_3 and reduced sulfur. Aromatic amino acids (Phe, Tyr, Trp) produce aromatic carboxylic

acids as a small fraction of the overall COD. Aromatic carboxylic acids are therefore not included in the ADM1. Ramsay (1997) compiled a spreadsheet of yields from amino acids to estimate the yields from the amino acid content of a protein substrate (Appendix D). Non-Stickland oxidation of amino acids may occur with low hydrogen or formate concentrations, or under thermophilic conditions, when oxidative reactions become more thermodynamically favourable, and oxidation reactions generally yield more propionate and less acetate and butyrate (in direct contrast to fermentation of monosaccharides). However, the use of a Stickland-based spreadsheet is a reasonable initial estimate of product yields. Because Stickland reactions are generally not inhibited by hydrogen, hydrogen regulation or inhibition functions have been excluded.

3.5 SYNTROPHIC HYDROGEN-PRODUCING ACETOGENESIS AND HYDROGEN-UTILISING METHANOGENESIS

Degradation of higher organic acids to acetate is an oxidation step, with no internal electron acceptor. Therefore the organisms oxidising the organic acid (normally bacteria) are required to utilise an additional electron acceptor such as hydrogen ions or carbon dioxide to produce hydrogen gas or formate respectively. These electron carriers must be maintained at a low concentration for the oxidation reaction to be thermodynamically possible (Figures 3.3 and 3.4, Table 3.4) and hydrogen and formate are consumed by methanogenic organisms (normally archaea).

The thermodynamics of syntrophic acetogenesis and hydrogen-utilising methanogenesis reactions are only possible in a narrow range of hydrogen or formate concentrations (and are also influenced to a lesser degree by other product and substrate concentrations). This is important for modelling, as the thermodynamic limitations largely determine the parameter for hydrogen inhibition, as well as half saturation coefficients and yields. The limitations are illustrated in Figure 3.3, which shows the thermodynamic yield ($\Delta G'$) for methanogenesis and three anaerobic oxidation reactions. The shaded region indicates where methanogenesis and propionate oxidation are simultaneously possible.

Table 3.4: Thermodynamics of reactions for fatty acid oxidising organisms.

Substrate	Reaction	ΔG^0 (kJ $gCOD^{-1}$)	$\Delta G'$ (kJ $gCOD^{-1}$)
H_2, HCO_3^-	$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$	–2.12	–0.19
Propionate	$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + 3H_2 + CO_2$	0.68	–0.13
Butyrate	$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2$	0.30	–0.16
Palmitate	$CH_3(CH_2)_{14}COOH + 14H_2O \rightarrow 8CH_3COOH + 14H_2$	0.55	–0.16

$\Delta G'$ Calculated for T 298 K, pH 7, pH_2 1×10^{-5} bar, pCH_4 0.7 bar, HCO_3^- 0.1M, and organic acids 1mM.

Figure 3.4 also demonstrates the relative importance of acetate concentrations, and hence aceticlastic methanogenesis as an acetate sink (vertical line on left of figure), by marking lines of zero $\Delta G'$ for varying acetate and hydrogen concentrations. The shaded region shows the space in which the five reactions are theoretical simultaneously possible. Note that the reactions are simultaneously possible over five orders of magnitude of acetate and only 2.5 orders of magnitude of hydrogen. Also shown in this figure is the measured threshold for methanogenesis (Cord-Ruwisch *et al.* 1988). This would more than halve the available operating space (remaining region above dotted line) and if the other reactions had similar limitations, a very narrow region of acetate and hydrogen levels would be available.

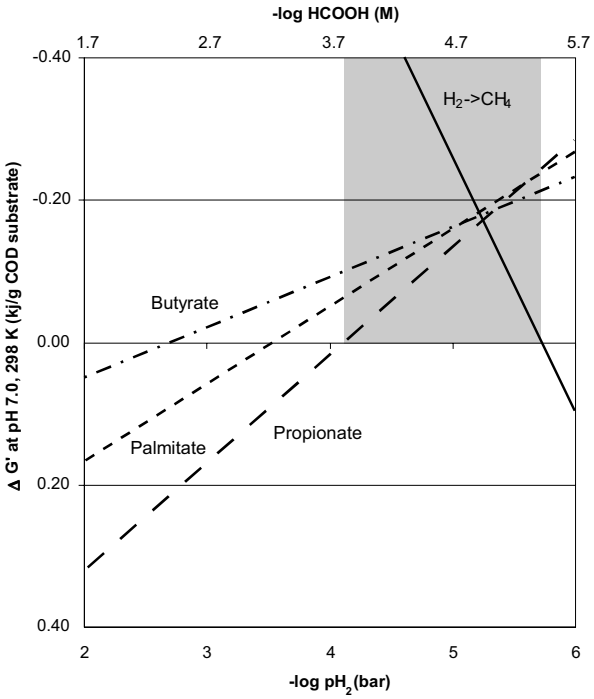

Figure 3.3: $\Delta G'$ for the reactions shown in Table 3.5 at different hydrogen partial pressures (bottom x-axis) and formate concentrations (top x-axis). Apart from hydrogen/formate, concentrations are 0.1M $HCO3^{-}$, and 1mM organic acids at pH 7. The shaded region shows the theoretical operating region for syntrophic acetogenesis from propionate. Valerate is thermodynamically similar to butyrate. ΔG^0 values are taken from Madigan (2000) and $\Delta G'$ calculated from $\Delta G' = \Delta G^0 - RT \ln ([C]^c [D])^d/([A]^a [B]^b)$ in the reaction: $aA + bB \Leftrightarrow cC + dD$.

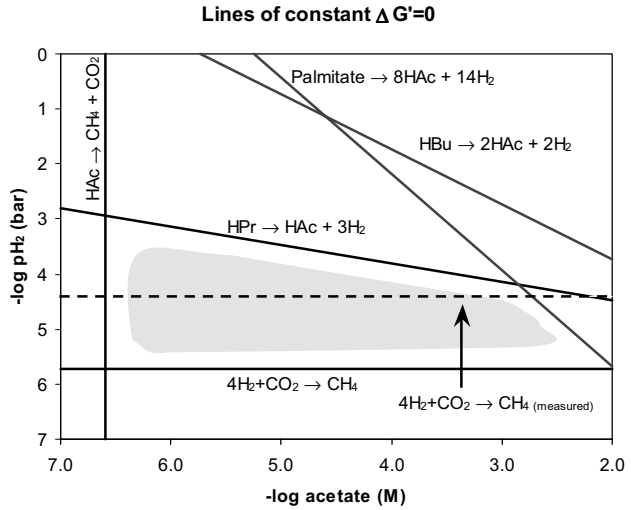

Figure 3.4: Lines of zero $\Delta G'$ (298 K) for five reactions with similar assumptions to those in the caption to Figure 3.3 (except acetic acid concentration). The shaded portion shows regions where all reactions are possible. The measured hydrogen-utilising threshold and corresponding line (- - -) are based on Cord-Ruwisch *et al.* (1988).

SULFATE REDUCTION AND SULFIDE INHIBITION

When oxidised sulfur compounds are present in anaerobic digesters, they will generally be reduced to S^{2-}. This is because the oxidised sulfur is reduced in thermodynamic and kinetic preference to hydrogen ions (to H_2) or CO_2 (to formate). Organisms reducing sulfur compounds can obtain the electrons directly by oxidising organic acids, or H_2. Additionally, organic acids are used as a carbon source and, as a result, organisms reducing sulfur compounds compete with the majority of other groups in anaerobic digestion including:

(1) Hydrogenotrophic organisms for hydrogen (at low levels of influent SO_x);
(2) Acetogenic and aceticlastic organisms for electrons and carbon (at medium levels of influent SO_x).

Further complicating the effect on anaerobic systems, the reduced product, sulfide, is inhibitory at 0.003–0.006 M total S, of which the fully associated form (H_2S) is the inhibitory agent, at levels of 0.002–0.003 M H_2S (Speece 1996). Hydrogenotrophic, acetogenic and aceticlastic organisms are all affected, and other groups including sulfate-reducing organisms (except perhaps acidogenic organisms) are inhibited by sulfide. Sulfide has a similar acid-base system to the inorganic carbon system, with S^{2-}, HS^- and H_2S as components. H_2S is also a gas phase component, with a relatively high solubility (0.1 M bar^{-1}). Solubility and acidity coefficients are strongly affected by temperature (Speece 1996), and the relationships are well described by the van't Hoff equation.

All anaerobic processes simulated by the ADM1, both biological and physico-chemical, except perhaps disintegration and hydrolysis, are affected by either competition for substrate, inhibition by H_2S, or the acid-base reactions and gas–liquid transfer of H_2S. Because of its complexity, the sulfate reduction system was not included in the ADM1. The ADM1 is therefore incapable of modelling systems with low to medium amounts of sulfide (>0.002 M influent SO_x). The simplest method of modifying the model to incorporate sulfate reduction at relatively low influent SO_x concentrations is to include, for example, an extra group of organisms degrading oxidised sulfur to reduced sulfides, with electrons and hydrogen sourced from hydrogen, and carbon for growth sourced from CO_2. The acid-base pair HS^-/H_2S should also be included, with transfer to the gas phase of H_2S. But generally, more complicated models, with different sulfate reducing groups describing competition for organic acids must be included (Kalyuzhnyi and Fedorovich 1998).

3.5.1 Form of electron carrier

The electron carrier can be either hydrogen (from hydrogen ions) or formate (from carbon dioxide). There are three major differences between the two forms ($H_2 + CO_2 \Leftrightarrow HCOOH$):

(1) Hydrogen has a higher diffusivity.
(2) Formate is more soluble.
(3) Formic acid is a stronger acid than carbon dioxide.

Therefore, when interspecies distances are short, hydrogen transfer will be faster and when distances are long, the greater solubility of formate allows a greater concentration gradient and therefore better transfer. Additionally, formic acid has a different influence on the physico-chemical system due to the lower pK_a compared to CO_2. Apart from this, model implementation is largely unaffected as stoichiometry and thermodynamics are virtually identical and hydrogen/formate may be in enzyme-assisted equilibrium (Thiele and Zeikus 1988). Also, acetogens may waste electrons as either hydrogen or formate and hydrogen-utilising methanogens can accept either (Boone *et al*. 1993). The task group therefore decided to implement the electron carrier as hydrogen only, and to not include formate.

3.5.2 Biological groups and components in the ADM1

The main pathway for anaerobic fatty acid degradation above propionate (C_3) is β-oxidation. This is a cyclic process where one acetate group is removed per cycle for a yield of 1/3 ATP per cycle (Finnerty 1988). The final carbon-containing product of fatty acids with even number of carbon atoms is acetate only. When the fatty acid has an odd number of carbon atoms (e.g. valerate, C_5), one mole of propionate is produced per mole of substrate. Most naturally occurring LCFA have an even number of carbon atoms (Gunstone 1996) and acetate can be regarded as the major carbon product from this substrate. The task group considered three main fatty acid substrates (above C_4) of importance: butyrate, valerate and LCFA. Butyrate and valerate are thought to be degraded by the same organisms (included as such in the ADM1) while long chain fatty acids have a dedicated biological group in the ADM1 because of the transport difficulties and different physico-chemical characteristics of these much larger molecules. Three acetogenic bacterial groups are therefore proposed, one for propionate, one for butyrate+valerate and one for LCFA ($>C_5$). A single group of organisms is included for hydrogen utilising methanogenesis. Homoacetogenesis and sulfate reduction are also potentially important sinks for hydrogen, especially under suitable conditions, but have not been included in the ADM1 (see boxes).

3.5.3 Hydrogen inhibition functions for acetogenesis

Free energies for both acetogenesis and hydrogenotrophic methanogenesis are very low and both microbial groups may use proton and cation motive forces for partial yields as opposed to substrate level phosphorylation. The task group discussed using a decreased yield at decreased free energy levels rather than a standard inhibition function. Another function considered was the thermodynamic inhibition model of Hoh and Cord-Ruwisch (1996), in which the equilibrium coefficient was used directly in a model to prevent reaction at thermodynamically unfavourable conditions. However, to reduce model complexity, and increase flexibility (e.g. for biofilm systems), the standard non-competitive inhibition function was preferred for hydrogen regulation in the ADM1. Liquid phase hydrogen concentration was used for hydrogen inhibition.

NITRATE REDUCTION

Dissimilatory nitrate reduction, a form of anaerobic respiration, is the reduction of NO_3^- to nitrogen oxides – such as NO_2^-, NO, and N_2. Because the production of gaseous nitrogen compounds leads to a decrease in the nitrogen concentration in the liquid phase, this process is also called *denitrification*. A wide variety of facultative prokaryotes perform dissimilatory nitrate reduction, most of them belonging to the Proteobacteria (Madigan *et al.* 2000). A number of obligate anaerobic, facultative anaerobic, and microaerophilic bacteria perform dissimilatory nitrate reduction to NH_4^+, mainly in carbon-rich, electron-acceptor-poor environments (Tiedje 1988). Organotrophic denitrifiers can use a wide range of natural organic substrates as carbon and electron sources, and have also been found to degrade several anthropogenic compounds (e.g. phenols and benzoates). In addition, several denitrifying bacteria can grow by fermentation. Although of lesser importance for treatment systems, lithotrophic denitrifiers – which can use H_2, S^o and H_2S as electron donors – and phototrophic denitrifiers exist. In anoxic systems, anaerobic ammonia oxidation (Anammox), in which NO_2^- is reduced to N_2 using NH_4^+ as the electron donor is mediated by certain autotrophic micro-organisms (Kuenen and Jetten 2001). The occurrence of this process in methanogenic systems is not well documented.

In the context of an organic matter fermenting, overall methanogenic system, nitrate reduction can have the following effects:

(1) Channelling of electron equivalents (eeq) away from methanogenesis, which results in an overall decrease in methane production. The reduction of one mole of NO_3^- to N_2 requires 5 eeq, whereas reduction to NH_4^+ requires 8 eeq:

$$NO_3^- + 6H^+ + 5e^- \rightarrow 0.5N_2 + 3H_2O$$
$$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$$

(2) Decrease in the methane content of the biogas as a result of the production of N_2 and additional CO_2 (resulting from electron donor oxidation and denitrification), as well as alkalinity and/or NH_4^+ production.

(3) Competition with other microbial groups for the same substrate(s). For example, denitrifiers would compete with methanogens for both acetate and H_2.

(4) Inhibition of methanogenesis by nitrogen oxides such as NO_3^-, NO_2^-, and N_2O (Klüber and Conrad 1998; Percheron *et al*. 1999).

Based on this brief discussion, in an overall methanogenic system, nitrate reduction can have a significant impact on both the carbon and electron flow, microbial competition and inhibition, and gas composition. Such interactions were deemed to be too complex for inclusion in the ADM. Inclusion of nitrate reduction in the model will require an additional microbial population (denitrifiers) with the corresponding kinetic parameters for substrate uptake (both organic compounds and NO_3^-), functions for partitioning of the total degradable substrate between fermentative/methanogenic and denitrifying populations, inhibition functions, etc. Although several of the steps could be regulated based on thermodynamic considerations (e.g. free energy), experimental data, kinetic data in particular, will be necessary for a more rational representation of simultaneous nitrate reduction and methanogenesis.

Syntrophic hydrogen producing and consuming organisms are often closely located and quite distinctive (Harmsen *et al.* 1996). Due to diffusion limitations, these syntrophic groups may locally regulate hydrogen, and bulk liquid and gas measurements of hydrogen or

formate concentrations may not necessarily directly reflect the concentrations within the syntrophic consortia. Initial testing of the model found that inhibitory hydrogen concentrations were 1×10^{-6} kgCOD m^{-3} liquid or 7×10^{-5} bar gas for propionate and 3.5×10^{-6} kgCOD m^{-3} liquid or 2×10^{-4} bar gas for butyrate and valerate (i.e. 50% inhibition at these levels, with gas–liquid equilibrium assumed), which agrees partly with the thermodynamic levels. Other studies of biofilm systems (Costello *et al.* 1991; Romli *et al.* 1995) have found hydrogen inhibition parameters an order of magnitude above the inhibitory level. Other conditions such as substrate concentrations, acetate concentration, pH, cation levels and weak acids could also decrease the thermodynamic inhibition level by increasing energetic maintenance requirements.

3.6 ACETICLASTIC METHANOGENESIS

In the major methanogenic step, acetate is cleaved to form methane and CO_2 (Eq. (3.3)).

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \Delta G^0 = -31 \text{ kJ} \times M^{-1} (\sim 0.25 \text{ ATP}) \qquad (3.3)$$

Two genera utilise acetate to produce methane (Madigan *et al*. 2000). *Methanosarcina* dominates above 10^{-3}M acetate while *Methanosaeta* dominates below this acetate level (Zinder 1993). *Methanosaeta* may have lower yields, higher k_m values, lower K_S values and be more pH-sensitive (Schmidt and Ahring 1996) as compared to *Methanosarcina. Methanosaeta* uses two moles of ATP to assist activation of one mole acetate (at low concentrations) while *Methanosarcina* only uses one (at higher acetate concentrations). Therefore, *Methanosarcina* has a greater growth rate while *Methanosaeta* needs a longer solids retention time, but can operate at lower acetate concentrations.

The presence of the two different organisms in anaerobic digesters is normally mutually exclusive with *Methanosaeta* often found in high rate (biofilm) systems (Harmsen *et al*. 1996; Sekiguchi *et al.* 1999) and *Methanosarcina* found in solids digesters (Mladenovska and Ahring 2000). Because of the exclusive nature of the system, the task group recommends that a single group of aceticlastic methanogens be used with different kinetic and inhibitory parameters depending on application and experimental observations.

3.7 INHIBITION AND TOXICITY

Speece (1996) uses two definitions within the area of general restriction of biological processes: ‘toxicity: an adverse effect (not necessarily lethal) on bacterial metabolism’ and ‘inhibition: an impairment of bacterial function’ (p. 246).

The word ‘bacterial’ should be expanded to ‘biological’, which includes other organisms (archaea, eucaryotes) and extracellular enzymes. The task group made the further definitions:

Biocidal inhibition: Reactive toxicity, normally irreversible, e.g. LCFA, detergents, aldehydes, nitro-compounds, cyanide, azides, antibiotics and electrophiles; defined by Speece (1996) as ‘toxicity’.

Biostatic inhibition: Nonreactive toxicity, normally reversible, e.g. product inhibition, weak acid/base (including VFA, NH_3 and H_2S) inhibition, pH inhibition, cation inhibition, and anything else that disrupts homeostasis; loosely defined by Speece (1996) as ‘inhibition’.

Forms of inhibition could be further separated into those that affect specific targets (e.g. detergents on cell membranes) and those that affect overall cell kinetics and function (e.g. pH inhibition).

WEAK ACID AND BASE INHIBITION

Free acid and base inhibition is the disruption of cell homeostasis by changes in pH, caused by passive transport of the free acid or base across the cell membrane, and subsequent dissociation (Henderson 1971). Because the relative amount of free acids or bases (compared to the ionic counterpart) is strongly pH-dependent, the inhibition is also pH-dependent, and the empirical pH inhibition functions may include the cumulative effect of free acid or base inhibition. Free acid or base pH inhibition is particularly important for organisms utilising substrate to product reactions with a low energy yield, or utilise proton motive forces, such as propionate and butyrate/valerate-oxidising organisms, and hydrogen and acetate-utilising methanogenic organisms. The following compounds are important as free acid or base inhibitory compounds (all pK_a values at 298 K):

(1) Free organic acids (HAc, HPr, HBu, HVa); main methanogenic precursors with pK_a values from 4.7–4.9. Mainly included in models as acetic acid inhibition.
(2) Free ammonia (NH_3); main free base in anaerobic digesters with a pK_a value of 9.25. Inhibition function included in the ADM1 for acetate utilisers.
(3) Hydrogen sulfide (H_2S); while it is known that the free form of H_2S is largely inhibitory as compared to HS^- or S^{2-} (Speece 1996), a pK_a of 7.05 would indicate the free acid buffers rather than disrupt homeostasis. In this case, the mechanism may be different.

Therefore, the free acids (associated organic acids, H_2S) cause inhibition at lower pH values, and free bases cause inhibition at higher pH values (NH_3). The organisms most affected by free acid and base inhibition are (in order of affect) aceticlastic methanogens, hydrogenotrophic methanogens and acetogenic organisms, though the last two are in a syntrophic consortia, and a decrease in activity of hydrogenotrophic methanogens will cause an apparent decrease in activity of organic oxidising organisms, due to the accumulation of hydrogen and formate.

In the ADM1, the effects of free organic acid inhibition are largely implicitly included in the empirical pH function, while the free ammonia inhibition is either implicitly included in the upper and lower empirical pH inhibition or explicitly included in the free ammonia inhibition function. H_2S inhibition is not included, since sulfate reduction is not included. As the major forms were implicitly included in other inhibition forms, free acid inhibition was not included. However, since the inhibition depends on the acid concentration as well as the pH, it is reasonable to include free organic acid inhibition when the concentration of free organic acids and pH fluctuate. Also, because the inhibition may occur by disruption of homeostasis, rather than decrease of activity or increase in cell death, the most appropriate function may be inhibition via decreased yield (see Table 3.5), rather than as decreased uptake rate via non-competitive inhibition.

Separation of biocidal and biostatic inhibition is important for modelling, as the first mainly influences biomass decay rate, while the second influences kinetic uptake and growth (maximum uptake, yield, half saturation parameters). Biostatic inhibition encompasses all the forms of inhibition included in the ADM1, is of most importance to anaerobic treatment, and is largely a result of the low yields available to anaerobic organisms. Most organisms that have an ATP yield of less than 1 mole/mole substrate or reaction cycle utilise cation or proton motive forces for anabolism rather than substrate level phosphorylation (Schink 1997). This is true of methanogenic archaea (Ferry 1993) and volatile fatty acid (VFA) oxidising organisms (Kleerebezem and Stams 2000). Weak acids and bases in free (non-ionic) form can pass through the cell membrane and dissociate, which disrupts proton motive force and homeostasis (Henderson 1971). At ion and pH levels away from the optimum, micro-organisms must expend energy to maintain homeostasis rather than for anabolism. Therefore, while product uptake may change very little, the yield decreases. This was recognised by Pirt (1965) who proposed a growth-independent maintenance coefficient. Increased energy use for maintenance limits the available energy for growth and, consequently, the biomass yield. Flexibility to include the different kinetic forms was one of the reasons the task group decided on an uptake-related kinetic equation rather than a growth-related kinetic equation as used in aerobic bioprocess models (e.g. Activated Sludge Model No. 1 (ASM1); Henze *et al.* 1987).

3.7.1 Modelling of inhibition

Several mechanisms of inhibition were considered, including the use of maintenance coefficients as a function of the inhibitor, in the maintenance-dependent kinetic rate equations proposed by Beeftink *et al.* (1990), based on Pirt's work (1965). While fundamentally sound, this approach was considered too complex and disparate from the Monod kinetics most commonly used. Inhibition kinetics considered by the task group are (see Table 3.5): (a) reversible forms as proposed by Lehninger (1975), of which non-competitive inhibition was used (extensively); (b) direct impact of the inhibitor on the microbial yield and decay (valuable, but not used in the ADM1); (c) two empirical forms used for pH inhibition (Angelidaki *et al.* 1993; Ramsay 1997); (d) competitive uptake, (which is not inhibition, but is included here for completeness); and (e) secondary substrate Monod kinetics, which are necessary to describe decrease in growth when nitrogen is limited (also not inhibition but included for completeness). More extensive reviews of inhibition and uptake/growth kinetics are presented by Pavlostathis and Giraldo-Gomez (1991), and Dochain (1986). Because the inhibition forms in anaerobic digestion are varied and extensive, the forms are expressed as in Eq. (3.4) where possible to allow for easy substitution or addition of inhibition terms:

$$\rho_j = \frac{k_m S}{K_S + S} X \cdot I_1 \cdot I_2 \cdots I_n \tag{3.4}$$

where the first part of the equation is the uninhibited Monod-type uptake, and $I_{1\ldots n} = f(S_{I,1\ldots n})$ are the inhibition functions (see Tables 3.1 and 3.2). Where this is not possible, because the inhibition function is integral in the uptake equation, the full uptake equation is shown in Table 3.5.

LCFA INHIBITION

Lipids constitute one of the main groups of organic matter and are found in domestic wastewater, organic household waste, agricultural waste and industrial waste. Indeed, special industrial wastes such as abattoir waste and waste from oil mills have a high lipids content. Triacylglycerols are the most abundant types of lipids and the major components of depot or storage lipids in plant and animal cells.

Triacylglycerols are represented as lipids in the ADM1. During anaerobic digestion, lipids are first hydrolysed to glycerol and long chain fatty acids (LCFA). This step is catalysed by extracellular enzymes called lipases. Hydrolysis of lipids proceeds rapidly compared to subsequent steps (Hanaki *et al.* 1981; Angelidaki and Ahring 1992). The resulting LCFA are degraded to acetate and hydrogen via activation and ß-oxidation. ß-oxidation of LCFA has been shown to occur under both mesophilic and thermophilic conditions (Weng and Jeris 1976; Angelidaki and Ahring 1995).

Long-chain fatty acids can be inhibitory at low concentrations (Henderson 1973; Hanaki *et al.* 1981; Roy *et al.* 1985; Rinzema *et al.* 1989; Koster and Cramer 1986; Angelidaki and Ahring 1992). In LCFA β-oxidising organisms, the LCFA are detoxified by activation with acyl-CoA to LCFA-CoA.

Several mechanisms of LCFA inhibition have been proposed:

(1) Growth inhibition by competitive inhibition of the synthesis of LCFA essential to the structure of new bacteria.
(2) Uncoupling of the electron transport chain from the proteins involved in ATP regeneration or transport of essential nutrients into the cell (Sheu and Freese 1972).
(3) Adhesion to the bacterial cell wall and restriction of the passage of essential nutrients (Henderson 1973).

It has been proposed that it is the associated form of LCFA that is inhibitory, and the inhibition is a result of LCFA adsorption on the cell surface. Therefore, factors such as cell surface area to LCFA concentration ratio, and pH may have an influence (Hwu *et al*. 1996). In general, heavy inhibition is irreversible (i.e. toxic), as recovery cannot be affected by a decrease in influent LCFA concentrations (Angelidaki and Ahring 1992; Hwu et al. 1996). While the most heavily inhibited organisms are probably aceticlastic methanogens, all organisms are inhibited to a varying degree (Hwu 1997; Angelidaki and Ahring 1992).

While LCFA may complicate the process by inhibition, adaptation may also occur, and a well developed process will readily degrade feeds with a high content of lipids. This is because efficient LCFA degradation (in an adapted culture) will be able to remove LCFA as fast as they are released from the hydrolysis of lipids. However, in order to avoid high transient concentrations of LCFA, gradual acclimation is required.

Therefore, LCFA inhibition can have a significant impact on process operation when fed lipid-rich waste, and the ADM1 cannot describe reactor behaviour under transient high LCFA concentrations, especially if toxic overload occurs. LCFA inhibition has not been included in the ADM1, because of the potential complexity of the inhibition and its lower frequency (as opposed to the commonly included inhibition functions). Models which include LCFA inhibition (for manure and oil degradation) have been presented by Angelidaki *et al*. (1999).

Table 3.5: Inhibition forms.

	Description	Equation	Used for	j[1]
(a)	Non-competitive inhibition	$I = \frac{1}{1+S_I/K_I}$	Free ammonia and hydrogen inhibition	7–12
	Uncompetitive	$\rho_j = \frac{k_m X S}{K_S + S\left(1+\frac{K_I}{S_I}\right)}$	Not used	
	Competitive	$\rho_j = \frac{k_m X S}{K_S\left(1+\frac{S_I}{K_I}\right)+S}$	Not used	
(b)	Reduction in yield	$Y = f(S_I)$	Not used	
	Increased biological decay rate	$k_{dec} = f(S_I)$	Not used	
(c)	Empirical upper and lower inhibition	$I = \frac{1+2\times10^{0.5(pH_{LL}-pH_{UL})}}{1+10^{(pH-pH_{UL})}+10^{(pH_{LL}-pH)}}$	pH inhibition when both high and low pH inhibition occur	5–12[2]
	Empirical lower inhibition only	$I = \exp\left(-3\left(\frac{pH-pH_{UL}}{pH_{UL}-pH_{LL}}\right)^2\right)\Big\|_{pH<pH_{UL}}$; $I = 1\Big\|_{pH>pH_{UL}}$	pH inhibition when only low pH inhibition occurs	5–12[2]
(d)	Competitive uptake	$I = \frac{1}{1+S_I/S}$	Butyrate and valerate competition for C_4	8–9
(e)	Secondary substrate	$I = \frac{1}{1+K_I/S_I}$	All uptake, to inhibit uptake when S_{IN}~0	5–12

Nomenclature: K_I = inhibition parameter; ρ_j = rate for process j; S = substrate for process j; S_I = inhibitor concentration; X = biomass for process j.

1. Processes where inhibition term used.
2. Only one pH inhibition term used, and form 1 (with upper and lower inhibition) should not be used with free ammonia inhibition. For the first pH function, pH_{UL} and pH_{LL} are upper and lower limits where the group of organisms is 50% inhibited respectively. For example, acetate-utilising methanogens with a pH_{UL} of 7.5 and a pH_{LL} of 6.5 have an optimum at pH 7. For the second function, pH_{UL} and pH_{LL} are points at which the organisms are not inhibited, and at which inhibition is complete respectively. Acetate-utilising methanogens with a pH_{UL} of 7 and a pH_{LL} of 6 will be completely inhibited below pH 6 and not inhibited above pH 7.

pH inhibition is a combination of disruption of homeostasis and increased weak acids concentration at low pH, or weak bases inhibition and transport limitations at high pH, and affects all organisms to some degree. pH inhibition is used for all intracellular processes in the ADM1 (I_{pH}), with different parameters for acetogens and acidogens, hydrogen-utilising methanogens and aceticlastic methanogens (see Chapter 6 for recommended values). Both the pH functions in Table 3.5 are useful for uptake equations, since the first form can be used in systems that are strongly buffered by ammonia or other bases (>pH 8), and the second is more flexible when low pH inhibition is likely to occur, for example, in carbohydrate systems. Hydrolysis may be inhibited at either low or high pH and is probably caused by partial denaturation of enzymes. Boon (1994) demonstrated the effect of batch digestion on primary sludge and showed an optimal hydrolysis at pH 6.8, but little significant change

between pH of 6.5 and 7.5. pH inhibition of hydrolysis was not included but, if required, functions are given in Veeken *et al.* (2000) and Sanders (2001).

Apart from pH inhibition, hydrogen inhibition of acetogenic bacteria (I_{H2}; see Section 3.5) and free ammonia inhibition of aceticlastic methanogens ($I_{NH3,Xac}$) are included in the ADM1, both described using non-competitive functions. Although potentially important, the biocidal effect of LCFA was not included (but is addressed in the accompanying box). Non-competitive inhibition was used in general, because it is the most commonly used form in the literature, which makes previously published inhibitory parameters directly applicable. However, other inhibition forms may be more suitable for (among others) hydrogen inhibition (Hoh and Cord-Ruwisch 1996) or organic acid inhibition (Mösche and Jördening 1999). More fundamental inhibition functions such as those in (b) above and an inhibition-independent maintenance coefficient with the kinetic rate equations of Beeftink *et al*. (1990) may also be more appropriate for biostatic inhibition in general (e.g. free acid, free base and hydrogen), but currently the pool of knowledge is too limited to allow such implementation.

3.8 INFLUENCE OF TEMPERATURE

Temperature can affect biochemical reactions in five main ways:

(1) Increase in reaction rates with increasing temperature (as predicted by the Arrhenius equation).
(2) Decrease in reaction rate with increasing temperature above optimum (>40°C for mesophilic and >65°C for thermophilic).
(3) Decrease in yields, and increase in Ks, due to increased turnover and maintenance energy with increased temperature.
(4) Shifts in yield and reaction pathway due to changes in thermodynamic yields and microbial population.
(5) Increase in death rate due to increased lysis and maintenance.

There are three major operating ranges nominally defined in anaerobic digestion: psychrophilic (4–15ºC), mesophilic (20–40ºC), and thermophilic (45–70ºC). While reactors can operate effectively between these ranges, optimal temperatures for mesophilic and thermophilic organisms are approximately 35ºC and 55ºC respectively (Figure 3.5).

The temperature dependence of the different groups of organisms follows the Arrhenius equation up to a temperature optimum, followed by a rapid drop to zero (Figure 3.5). The task group recognised three major system types that may need modelling with respect to temperature:

(1) *Temperature controlled with small changes in operating temperature (±3ºC)*: This can be modelled without temperature dependency, though parameters should be sourced or fitted for the operating temperature. This includes the majority of applications.
(2) *Uncontrolled but fluctuating within one range (either mesophilic or thermophilic)*: This can be modelled with a double Arrhenius equation in k_m that describes the rapid decrease at the higher temperatures (given in Pavlostathis and Giraldo-Gomez (1991); from Hinshelwood (1946)).

(3) Fluctuations between mesophilic and thermophilic temperatures: Regular changes in population and reaction pathways between mesophilic and thermophilic conditions is a complex scenario that is outside the scope of this report. Additionally, a system operating in this way will not be effective.

ACETATE OXIDATION

Acetate oxidation is the first step of a two-step reaction in which acetate is first oxidised to H_2/CO_2 (Eq. (1) below), and subsequently converted to CH_4 (Eq. (2)) (Zinder and Koch 1984). This reaction is performed by an acetate-oxidising bacterium in a syntrophic association with a hydrogenotrophic methanogen:

$$CH_3 - COO^- + 4H_2O \rightarrow 4H_2 + 2HCO_3^- + H^+ \qquad \Delta G^{\circ\prime} = +104 \text{ KJ/mol} \qquad (1)$$

$$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O \qquad \Delta G^{\circ\prime} = -135 \text{ KJ/mol} \qquad (2)$$

The high Gibbs free energy for the acetate oxidation reaction ($\Delta G^{\circ\prime}$ = +104 kJ/mol) might suggest that the contribution of syntrophic acetate conversion to the overall digestion process is not very important compared to aceticlastic methanogenesis. Under specific stress conditions, or those that favour acetate oxidation over other forms of acetate removal, such as high temperature, its importance is considerably magnified. Petersen and Ahring (1991) demonstrated that syntrophic acetate oxidation might contribute up to 14% of total acetotrophic methanogenesis in a thermophilic (60°C) digester.

At temperatures between 50°C and 65°C, the predominant degradation pathway for acetate depends largely on the acetate concentration. At low acetate concentrations, the acetate oxidation pathway is important whereas at high acetate concentrations the aceticlastic reaction (Eq. (3.3) is the preferred pathway (Zinder and Koch 1984; Petersen and Ahring 1991). At temperatures higher than 65°C, the syntrophic acetate oxidation is the predominant pathway as it is beyond the temperature range of the aceticlastic methanogens (Lepisto and Rintala 1999).

In the ADM1 it is considered that the majority of acetate will be degraded via the aceticlastic reaction. Nevertheless, in the case of extreme thermophilic processes (T > 65°C) or thermophilic treatment (45°C < T < 65°C) at low acetate concentrations, the acetate oxidation pathway may be included. It may be appropriate to include the acetate oxidation (see Eq. (1) above) as a separate process into the ADM1, since organisms mediating hydrogen utilising methanogenesis are currently included. However, published kinetic parameter values are generally for the acetate oxidising co-culture (homoacetogenic bacterium and hydrogenotrophic methanogen; Zinder and Koch (1984); Lepisto and Rintala (1999)), which means that parameters must be estimated if the two processes are separated. A model including acetate oxidation is also dependent on the electron sink. Electron acceptor end products such as hydrogen and formate are accounted for but, when sulfate is present, the system is further complicated. When SO_4^{2-} is the final electron acceptor, the produced H_2 can alternatively be used by sulfate-reducing bacteria. The latter organisms generally have a much higher affinity for H_2 than do methanogens. In the ADM1 sulfate reduction is not currently included and modelling of thermophilic digestion of wastewaters containing sulfate therefore requires considerable modifications.

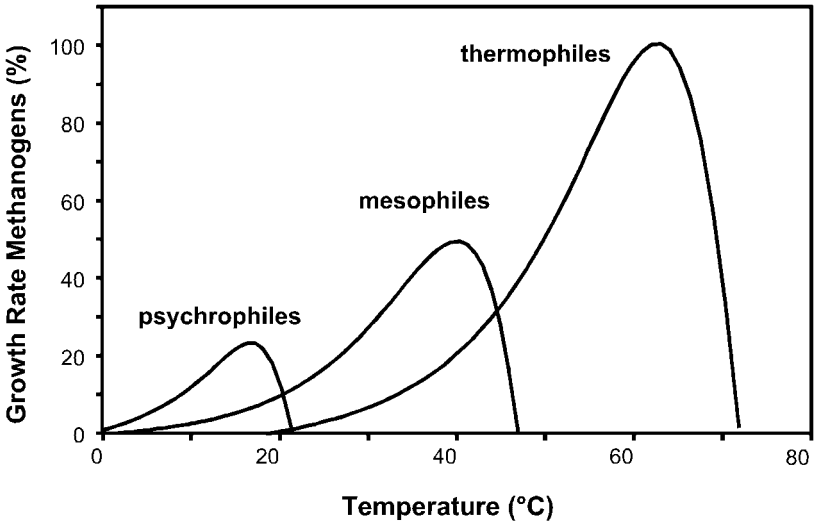

Figure 3.5: Relative growth rate of psychrophilic, mesophilic and thermophilic methanogens (from van Lier *et al.* 1997, reproduced with permission).

An empirical equation that effectively demonstrates the combined influence of temperature on the kinetic parameters was given by Pavlostathis and Giraldo-Gomez (1991) via reviewed parameters for the minimum solids retention time versus temperature in primary sludge digesters (Eq. (3.5)).

$$SRT_{min} = \left(0.267 \times 10^{(1-0.015(308-T))} - 0.015\right)^{-1} \tag{3.5}$$

where T is the temperature in K, and SRT_{min} is the minimum solids retention time to avoid washout.

Although yield and decay rates are affected by temperature, it was decided not to use continuous functions but instead to use separate values for thermophilic and mesophilic conditions.

3.8.1 Modelling of temperature effect on disintegration and hydrolysis

Temperature has an effect on both disintegration and hydrolysis. Changes in disintegration rates and first order hydrolysis rates (with the exception of lipids, due to physico-chemical characteristics) can be described using the Arrhenius equation (Sanders 2001).

3.8.2 Effect of temperature on thermodynamic yields and reaction pathways

Temperature has an effect on all reaction thermodynamics, which can be described by the Van't Hoff equation. In general, oxidative reactions become more favourable at higher temperatures (van Lier 1995), and the temperature dependence of the homoacetogenesis/ acetate oxidation (forward/reverse) reactions (see Figure 3.6) is probably the most important.

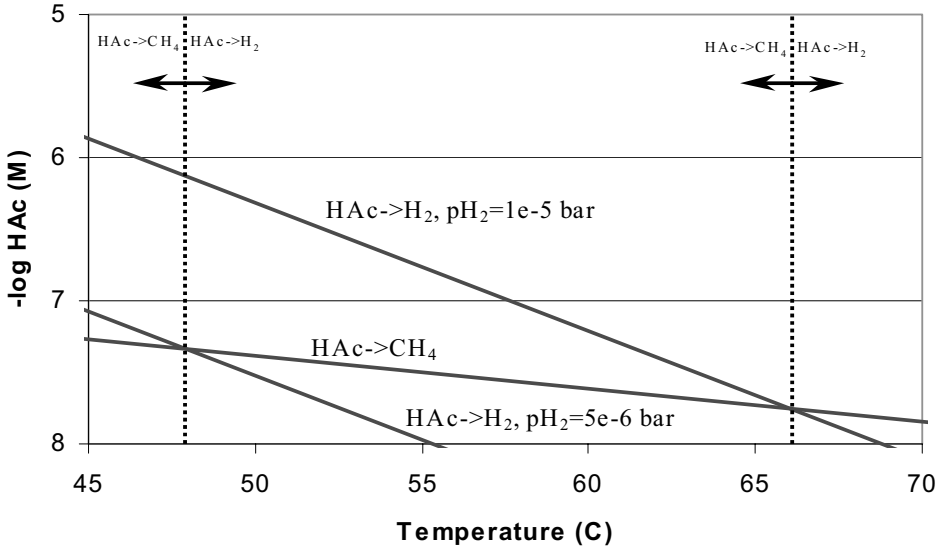

Figure 3.6: Lines of constant $\Delta G' = 0$ for acetate cleavage ($HAc \rightarrow CH_4$) and acetate oxidation ($HAc \rightarrow H_2$), at two different hydrogen concentrations; CO_2 and H_2O not shown. The dotted lines indicate regions where both reactions are equally possible. To the left of the lines, acetate cleavage is favoured. To the right, acetate oxidation is favoured. $\Delta G^0|_{298K} = -105$ kJ/mole and $\Delta H^0 = -232$ kJ/mole.

Homoacetogenesis is favoured at psychrophilic temperatures (see box), while acetate oxidation becomes more favourable at higher temperatures. At mesophilic conditions homoacetogenesis is normally outcompeted for molecular hydrogen by hydrogenotrophic methanogens, while acetate oxidation is normally outcompeted for acetate by *Methanosaeta* or *Methanosarcina*, except under unusual conditions (e.g. Schnürer *et al.* 1999).

Though homoacetogenesis and acetate oxidation may be significant under psychrophilic (Rebac *et al.* 1995) and thermophilic (Zinder and Koch 1984) conditions, respectively, the task group considered that the majority of hydrogen and acetate would continue to be converted directly to methane, and that alternate pathways should not be included in this version of the model (though they are addressed in boxes).

HOMOACETOGENESIS

The characteristic property of homoacetogenic bacteria is their ability to use carbon dioxide and to reduce it with molecular hydrogen via the carbon monoxide dehydrogenase system to acetate as an end-product (Schink 1994). Growth with H_2 and CO_2 according to the reaction

$$4H_2+2CO_2 \rightarrow CH_3COOH + 2H_2O, \qquad \Delta G^o = -95 \text{ kJ}$$

has been reported for nearly all homoacetogens. Homoacetogens are one of the most versatile physiological groups among the anaerobic bacteria. They utilise and transform one-carbon compounds and can carry out incomplete oxidation of reduced fermentation products released by other fermenting bacteria. Homoacetogens can use various substrates sequentially or simultaneously and may constitute an energy link from hydrogen, via acetate to heterotrophic methanogens. Most known homoacetogenic bacteria were isolated from strictly anoxic environments. *Clostridium thermoaecticum* and *Acetobacterium woodii* are examples of such organisms.

At mesophilic conditions, homoacetogens have much higher H_2 threshold levels (520–950 ppm) than sulfate-reducers and methanogens. Therefore, they are usually considered to be non-dominant in anaerobic digesters (Zhang and Noike 1994). However, below 20°C, homoacetogens can play a significant part in hydrogen oxidation because of the low activity of methanogenic organisms at low temperatures (Conrad *et al*. 1989). Homoacetogens are relatively fast-growing bacteria (Lokshina and Vavilin 1999). Inclusion of a homoacetogenic population in the ADM1 would require that competition be described between hydrogenotrophic methanogenic and homoacetogenic organisms for H_2 and CO_2 as described by Vavilin *et al.* (2000). Because the homoacetogenic bacteria can carry out oxidation of other reduced fermentation products, such reactions should also be considered in an extended model.

4

Physico-chemical processes

The physico-chemical system can be defined as non-biologically mediated processes that commonly occur in anaerobic reactors. There are three broad types listed below according to the relative kinetic rates (i.e., relative to the biochemical rates):

(1) Liquid–liquid processes (i.e. ion association/dissociation: rapid)
(2) Liquid–gas processes (i.e. liquid–gas transfer: rapid/medium)
(3) Liquid–solid processes (i.e. precipitation/solubilisation: medium/slow).

Only the first two process types have been commonly addressed in anaerobic models, likely because of the difficulties in implementation of liquid–solid processes, and solids precipitation has not been included in the ADM1 (see box). However, it may be important in systems with cations which readily form precipitates such as Ca^{2+} and Mg^{2+} (see box). Correction for non-ideal behaviour of ions, which potentially influences all physico-chemical processes was not included in the ADM1. Therefore in systems with medium/high levels of ions, and especially where effluent is recycled to upstream processes, the ion activity coefficient should be calculated and, if necessary, corrections applied (Stumm and Morgan 1996; Musvoto *et al.* 2000a).

The physico-chemical system is very important when modelling anaerobic systems because:

- a number of biological inhibition factors can be expressed (such as pH, free acids and bases, concentrations of soluble gases in the liquid phase);
- major performance variables such as gas flow and carbonate alkalinity are dependent on correct estimation of physico-chemical processes;

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- often the major operating cost is pH control with a strong acid or base. In this case, the control setpoint (pH) and inputs are calculated from physico-chemical estimation.

4.1 LIQUID–LIQUID PROCESSES

This section discusses ion association and dissociation with hydrogen and hydroxide ions. There are a number of important compounds, which have pK_a values (dissociation coefficients) close to the operating pH of anaerobic systems (Table 4.1). Organic acids have pK_a values of approximately 4.8, the $CO_{2(aq)}/HCO_3^-$ acid-base pair has a pK_a of 6.35 while the NH_4^+/NH_3 acid-base pair has a pK_a of 9.25. The base CO_3^{2-} is in very low concentrations as the acid-base pair HCO_3^-/CO_3^{2-} has a pK_a of 10.3, and CO_3^{2-} was therefore excluded from the model (all pK_a values for 298 K).

The $CO_{2(aq)}$ to HCO_3^- reaction passes through H_2CO_3, a relatively strong acid ($pK_a = 3.5$). However, the equilibrium coefficient for $[CO_{2(liq)}]/[H_2CO_3]$ is 631 (298 K; Stumm and Morgan 1996), which means that $[CO_{2(liq)}] >> [H_2CO_3]$ and $CO_{2(liq)}$ can be taken as the effective acid.

Because association/dissociation processes are so rapid (Musvoto *et al.* 2000a), they are often referred to as equilibrium processes and can be represented by an implicit set of algebraic equations. The species considered important and their equilibrium coefficients are shown in Table 4.1.

Table 4.1: Acid-base equilibrium coefficients (pK_a).

Acid/base pair	pK_a (298 K)	$\tilde{\Delta}H^0$ (J.mole^{-1})	$\theta(= \Delta H^0/(RT_1^2))$; T_1 = 298 K
CO_2/HCO_3^-	6.35[1]	7646	0.010
NH_4+/NH_3	9.25[1]	51965	0.070
H_2S/HS	7.05[1]	21670	0.029
$H_2O/(OH^- + H^+)$	14.00[1]	55900	0.076
HAc/Ac^-	4.76[2]	Maximum of 4.81 at 333K[3]	n/a
HPr/Pr^-	4.88[2]	Maximum of 4.94 at 333K[3]	n/a
$n\text{-}HBu/Bu^-$	4.82[2]	Maximum of 4.92 at 333K[3]	n/a
$i\text{-}HBu/Bu^-$	4.86[2]	No other data	n/a
$n\text{-}HVa/Va^-$	4.86[2]	No other data	n/a
$i\text{-}HVa/Va^-$	4.78[2]	No other data	n/a

1. Lide (2001).
2. Sillen and Martel (1964).
3. Does not fit constant enthalpy form of van't Hoff (Eq. (4.10)).

4.1.1 Modelling of acid-base reactions

Implementation of the equations describing acid-base reactions depends on whether they are formulated and solved as differential equations or an implicit algebraic set of equations. This is further described in Chapter 5, and the equations given in detail in Appendix B. In either case, two approaches can be taken to formulate the equations: the charge balance or the tableau method (Morel and Hering 1993). The task group recommends that the charge balance is used because it is easier to understand and has greater educational value. However, the tableau method can be used to improve the numeric structure of the algebraic equations for implicit algebraic or differential implementation. The charge balance can be expressed as:

SOLIDS PRECIPITATION

Solids precipitation is the complexing of cations and anions in neutral inorganic solid form. Potentially important solid precipitants in anaerobic digesters include calcium carbonate ($CaCO_3$, pK_{so} = 8.2 – 8.5), calcium phosphate ($CaPO_4$) magnesium carbonate ($MgCO_3$, pK_{so} = 7.5 – 8.2), the metal sulfide precipitates (particularly FeS and Fe_2S_3) and magnesium-phosphate complexes such as struvite ($MgNH_4PO_4$) and newberyite ($MgHPO_4$) (Musvoto *et al.* 2000a). Modelling metal sulfide precipitation is mainly of importance when sulfate reduction is modelled, and when $Fe^{2/3+}$ is added to precipitate the resulting sulfide, an expensive option that is becoming less popular. This is therefore not addressed here. The most important form of precipitate is $CaCO_3$ (van Langerak 1998), because of the large amounts of Ca^{2+} in pulp and paper wastewaters, to which anaerobic treatment is often applied. The magnesium precipitates are of particular importance when the influent is high in Mg^{2+}, or $Mg(OH)_2$ is used to raise pH. The acid/base system $Mg^{2+}/MgOH^{+}/Mg(OH)_2$, and magnesium-phosphate derivatives must also be considered under these circumstances. Because of the complexity of the Mg^{2+} system, and because the $CaCO_3$ system can be used to illustrate common complications, this is addressed specifically here.

Formation of the solid phase is a complicated process that depends heavily on kinetics as well as thermodynamics. The three processes are nucleation, crystallisation, and ripening (van Langerak 1998). The second two processes are surface-related, which causes the rate at which they occur to be dependent on the surface area (and hence concentration) of the solid phase. Additionally, a number of additives can affect these processes (for example, phosphate inhibits the formation of $CaCO_3$ precipitates; van Langerak 1998). There may be a number of different precipitates, with the same empirical formula, depending on precipitation rate, thermodynamics and temperature. In particular, $CaCO_3$ can either be amorphous (forms faster and at lower ion concentrations) or crystalline.

The main reason for excluding precipitation kinetics from the ADM1 was the complexity of the process, the range of different precipitating cations (and larger number of products), and because systems which have high levels of Ca^{2+} and Mg^{2+} are relatively limited (see above). However, in order to model the physico-chemical characteristics of these systems effectively, some form of precipitation mechanism should be included. Excluding the precipitation process while including the Ca^{2+} ions as cations would cause: (1) the model to incorrectly predict pH, because of ion precipitation; (2) the model to over-predict gas carbon dioxide and liquid inorganic carbon concentrations, since inorganic carbon is complexed during precipitation; and (3) faster physico-chemical dynamics in the model in general, since the system is dynamically buffered by the pool of $CaCO_3$, with slow precipitation kinetics. These are particularly important in high-rate anaerobic digesters, where the precipitated solids are retained together with biological solids. Additionally, it may be of value to include a precipitation process in order to assess the extent of ion precipitation, evaluate inorganic solids inventory and design new processes (e.g. van Langerak and Hamelers 1997).

Methods for including precipitation are given by Musvoto *et al.* (2000a,b), and van Langerak and Hamelers (1997), but the simplest method, for a single precipitant, is to include the precipitation process as an equilibrium reaction, or with first order kinetics. When a number of precipitant products are present, or the research or operational question is heavily oriented towards the kinetics of precipitation and the physico-chemical processes, a more complicated precipitation kinetic system should be implemented.

$$\sum S_{C^+} - \sum S_{A^-} = 0 \tag{4.1}$$

ΣS_{C^+} represents the total cationic equivalents concentration and ΣS_{A^-} the total anionic equivalents concentration. The equivalent concentration of each ion is its valence multiplied by molar concentration.

Implemented in the ADM1, the charge balance is as follows (denominators for organic acids represent the gCOD content per charge):

$$S_{Cat^+} + S_{NH_4^+} + S_{H^+} - S_{HCO_3^-} - \frac{S_{Ac^-}}{64} - \frac{S_{Pr^-}}{112} - \frac{S_{Bu^-}}{160} - \frac{S_{Va^-}}{208} - S_{OH^-} - S_{An^-} = 0 \tag{4.2}$$

where S_{Cat^+} and S_{An^-} represent metallic ions such as Na^+ and Cl^- and are included to represent strong bases and acids respectively (as well as, for example, the saline counter ions of NH_4^+ and HCO_3^- in added NH_4Cl and $NaHCO_3$). S_{Cat} and S_{An} can be treated as otherwise inert compounds with no consumption or reaction terms. Long chain fatty acids (LCFAs) were not included in the acid-base system because the number of charged sites per COD is so small. However, if free LCFA inhibition is to be used, or the LCFA concentration is high, they must be included in a similar manner to volatile fatty acids (VFA). Amino acid acid-base reactions were also not included, because of their low in-reactor concentrations (due to high acidogenesis rates), and because of the wide range of amino acid pK_a values (Ramsay 1997).

If the acid-base equations are implemented as an algebriac set, the combined concentration of the acid-base pair should be expressed as a dynamic state variable. For the inorganic carbon ($CO_{2,aq}/HCO_3^-$ pair), this state is as follows:

$$S_{IC} - S_{CO_2} - S_{HCO_3^-} = 0 \tag{4.3}$$

The remaining algebraic equations can be formulated from acid-base equilibria equations (for example, the $CO_{2,aq}/HCO_3^-$ pair):

$$S_{HCO_3^-} - \frac{K_{a,CO_2} S_{IC}}{K_{a,CO_2} + S_{H^+}} = 0 \tag{4.4}$$

where K_{a,CO_2} is the equilibrium coefficient. Likewise, for organic acids, and inorganic nitrogen:

$$S_{VFA^-} - \frac{K_{a,VFA} S_{VFA,total}}{K_{a,VFA} + S_{H^+}} = 0 \tag{4.5}$$

$$S_{NH_4^+} - \frac{S_{H^+} S_{IN}}{K_{a,NH_4} + S_{H^+}} = 0 \tag{4.6}$$

and hydroxide:

$$S_{OH^-} - \frac{K_w}{S_{H^+}} = 0 \tag{4.7}$$

Therefore, when acid-base reactions are implemented as an implicit algebraic equation set, the free form (e.g. S_{CO2}) and ionic form (e.g. S_{HCO3-}) are lumped together as a single dynamic state variable (e.g. $S_{IC} \equiv S_3$). The concentration of the free form of the acid-base pair only needs calculation (using the form of Eq. (4.3)) if it is used elsewhere in the model. In the ADM1, the free acids or bases calculated are S_{CO2} and S_{NH3}. If the liquid phase physico-chemical equations are implemented as differential equations, the free and total forms are implemented as dynamic state variables, the lumped dynamic form (e.g. S_{IC}) is redundant, and an additional kinetic rate equation is used for acid-base reactions (see Section 5.3). The biochemical production rates shown in Tables 3.1 and 3.2 can be either in the acid dynamic state variable or the base dynamic state variable (but not both), though we recommend having the rate equations in the free form (i.e. CO_2, HAc, etc.). Equation 4.7 (for S_{OH-}) should be substituted into the charge balance, and S_{H+} becomes a single unknown in a single equation (the charge balance). Therefore the algebraic equation set is explicit. A mixed solution method can also be used, with a number of the physico-chemical reactions implemented as kinetic rate equations, and the rest as an implicit algebraic equation set. Appendix B contains full equation sets for DAE and DE implementations.

4.2 LIQUID–GAS TRANSFER

The following three main gas components were considered significant as intermediates and as having a strong effect on biological processes or outputs (solubility values at 25°C):

H_2 – relatively low solubility (0.00078 $M_{liq}\,bar_{gas}^{-1}$)
CH_4 – relatively low solubility (0.0014 $M_{liq}\,bar_{gas}^{-1}$)
CO_2 – relatively high solubility (0.035 $M_{liq}\,bar_{gas}^{-1}$)

Other potentially important gases include H_2S, which was not included because sulfate reduction was also not included as a biochemical process, and ammonia, which is so soluble (K_H = 50 $M_{aq}\,bar_{gas}^{-1}$; Stumm and Morgan 1996) that the mass flux to gas is negligible compared to that in the effluent.

4.2.1 Liquid–gas transfer equations

Gas and liquid phases in contact will reach steady state with respect to each other. When the liquid phase is relatively dilute, Henry's law can be used to describe the equilibrium relationship. Henry's law is commonly expressed as the concentration in the liquid phase due to a gas phase partial pressure:

$$K_H p_{gas,i,ss} - S_{liq,i,ss} = 0 \tag{4.8}$$

where $S_{liq,i,ss}$ is the steady-state liquid phase concentration for component i (M); $p_{gas,i,ss}$ is the steady-state gas phase partial pressure of component i (bar); and K_H is the Henry's law coefficient ($M\,bar^{-1}$).

Resistance to transfer of relatively insoluble gases such as carbon dioxide, methane and hydrogen is mainly in the liquid phase (Coulson and Richardson 1993; Pauss *et al.* 1990). Pauss *et al.* (1990) showed that gases in anaerobic digesters may be supersaturated to a significant degree in relation to effluent organics and total COD balance. Therefore, dynamic gas transfer equations should be used to describe liquid–gas transfer. The most common equations follow the two-film theory of Whitman (1923). Derivation is described by Stumm and Morgan (1996) and the mass flux is a combination of the driving force and the rate equation (Eq. (4.9)).

$$\rho_{T,i} = k_L a(S_{liq,i} - K_H p_{gas,i}) \tag{4.9}$$

where k_La is the overall mass transfer coefficient multiplied by the specific transfer area (d^{-1}) and $\rho_{T,i}$ is the specific mass transfer rate of gas i. Note that each $\rho_{T,i}$ is an additional kinetic rate equation (in addition to those in Tables 3.1 and 3.2). It is necessary to correct K_H for H_2 and CH_4 by a factor of 16 and 64 respectively to account for the COD basis of $S_{H2/CH4}$ as compared to the molar basis of K_H. Because transfer of all three gases are liquid film controlled, and the diffusivities are similar, they should have k_La values of a similar order of magnitude. Values for k_La vary a great deal depending on mixing, temperature and liquid properties and, for simplicity, we recommend using the same k_La value for all three gases. This can be estimated using relationships to estimate k_La of O_2 in aerobic systems (which is also liquid film controlled; Tchobanoglous and Burton 1991; diffusivities given in Table 4.2) or, in systems producing medium to large amounts of gas, set an order higher than the fastest biochemical process for pseudo-equilibrium.

Table 4.2: Liquid–gas transfer parameter values.

Gas	K_H (298 K) [1] $M_{liq}\ bar_{gas}^{-1}$	ΔH^0 (J mole^{-1})	$\theta(=\Delta H^0/(RT_1^2))$; T_1 = 298 K	Diffusivity[2] at 298 K ($(m^2\ s^{-1}) \times 10^9$)
H_2	0.00078[3]	–4180	–0.00566	4.65
CH_4	0.0014[3]	–14,240	–0.01929	1.57
CO_2	0.035	–19,410	–0.02629	1.98

1. Lide (2001)
2. Pauss *et al.* (1990)
3. Multiply by a factor of 16 (H_2) and 64 (CH_4) to change K_H from M bar^{-1} to kgCOD m^{-3} bar^{-1}.

4.3 VARIATION OF PHYSICO-CHEMICAL PARAMETERS WITH TEMPERATURE

Changes in temperature have a fundamental influence on the physico-chemical system, mainly because of changes in equilibrium coefficients. The overall effect on the system due to changes in physico-chemical parameters with temperature is generally more important than that due to changes in biochemical parameters. The van't Hoff equation describes the variation of equilibria coefficients with temperature, and the task group chose it because of its fundamental basis. Derivation and further details are given in Stumm and Morgan (1996) and Puigdomenech *et al.* (1997). If ΔH (heat of reaction) is assumed independent of temperature, the van't Hoff equation can be integrated to Eq. (4.10), where ΔH^0 is heat of reaction at standard temperature and pressure, R, the gas law constant, K_1 is the known equilibrium coefficient at reference temperature T_1 (K) and K_2 is the unknown coefficient at T_2 (K).

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{4.10}$$

Note that a value of R equal to 8.324 J mole^{-1} K^{-1} should be used to be consistent with units of J mole^{-1} and K. Alternatively, if it is assumed that $T_1 \times T_2 \approx T_1^2$ and θ is substituted for $(\Delta H^0/(RT_1^2))$, Eq. (4.10) reduces to the following commonly used form (Siegrist *et al.* 1993; Angelidaki *et al.* 1999; Vavilin *et al.* 1997):

$$K_2 = K_1 e^{\theta(T_2 - T_1)} \tag{4.11}$$

Between 273 K (0°C) and 333 K (60°C), Eq. (4.10) is effective for all equilibrium coefficients in Tables 4.1 and 4.2, except the organic acids. However, the K_a values for the organic acids vary by a small amount in this temperature range, and can be assumed to be constant.

5

Model implementation in a single stage CSTR

This chapter describes implementation in a continuous-flow stirred-tank reactor (CSTR), although the equations will also describe batch and semi-batch mixed reactors. The formulated equations depend on whether the acid-base reactions are implementated as a implicit algebraic equation set or a number of additional kinetic rate and differential equations. In the first case, solution requires a differential and algebraic equation (DAE) solver. In the second, only a differential equation (DE) solver is required, but the differential equation set is stiffer, and an increased number of errors are introduced.

This section deals with implementation as a DAE system, with notes related to implementation as a DE system. The system demonstrated here is a constant volume completely mixed system (Figure 5.1). Included is a simple, but limited method for modelling the extended retention times found in biofilm systems, but a different hydraulic model is required for more complex systems such as solid phase digestion. The biochemical model matrix (see Tables 3.1 and 3.2) and the supplemental tables in Appendix B can also be used in more complex models.

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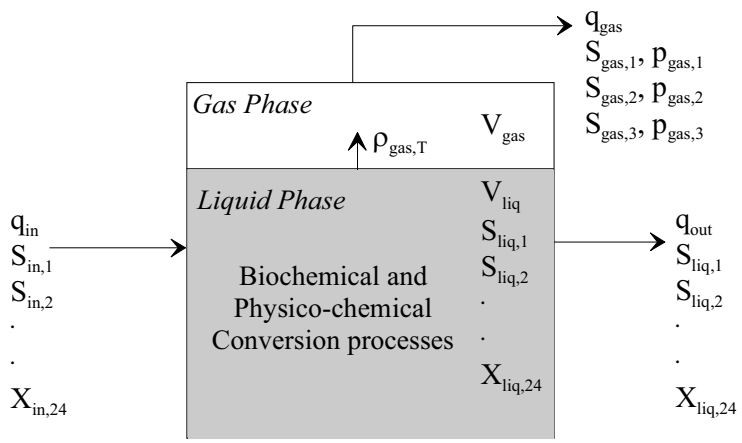

Figure 5.1: Schematic of a typical, single-tank digester. q = flow, $m^3 \times d^{-1}$ V = volume, m^3; $S_{stream,i}$ = concentration of soluble components; $X_{stream,i}$ = concentration of particulate components (all in kgCOD m^{-3}); i is the component index (see Tables 3.1 and 3.2).

5.1 LIQUID PHASE EQUATIONS

For each state component, the mass balance can be written as in Eq. (5.1).

$$\frac{dVS_{liq,i}}{dt} = q_{in}S_{in,i} - q_{out}S_{liq,i} + V\sum_{j=1-19}\rho_j\nu_{i,j} \tag{5.1}$$

where the term $\sum_{j=1-19}\rho_j\nu_{i,j}$ is the sum of the specific kinetic rates for process j multiplied by $\nu_{i,j}$ (Tables 3.1 and 3.2). If a constant volume is assumed ($q = q_{in} = q_{out}$), the expression can be in $S_{liq,i}$ as in Eq. (5.2). If the volume is not constant with time, it is also a dynamic state variable, and the chain rule must be used to express the concentration dynamic state equations in $dS_{liq,i}/dt$.

$$\frac{dS_{liq,i}}{dt} = \frac{qS_{in,i}}{V_{liq}} - \frac{qS_{liq,i}}{V_{liq}} + \sum_{j=1-19}\rho_j\nu_{i,j} \tag{5.2}$$

If the residence time of the concentration state is variable, for example, solids in biofilm or high-rate reactors, the retention time can be extended by replacing the second term (mass flow out) as in Eq. (5.3).

$$\frac{dX_{liq,i}}{dt} = \frac{qX_{in,i}}{V_{liq}} - \frac{X_{liq,i}}{t_{res,X} + V_{liq}/q} + \sum_{j=1-19} \rho_j \nu_{i,j} \tag{5.3}$$

where $t_{res,X}$ is the residence time of solids components above hydraulic retention time (that is: if $t_{res,X} = 0$, the overall solids retention time (SRT) is V_{liq}/q) to simulate separate solids retention (d). This is not a perfect implementation, as biofilm systems are very complex, and more fundamental solids retention models have been published by Bolle *et al.* (1986) and Buffiere *et al.* (1998). However, implementation of these models is beyond the scope of this report.

In addition to the rate equations in Tables 3.1 and 3.2, the following liquid/gas transfer kinetic rates (liquid volume-specific) for S_{H2}, S_{CH4} and S_{IC} (or S_{CO2}, depending on implementation) must be added:

$$\rho_{T,H_2} = k_L a(S_{liq,H_2} - 16\, K_{H,H_2} p_{gas,H_2}) \tag{5.4a}$$

$$\rho_{T,CH_4} = k_L a(S_{liq,CH_4} - 64\, K_{H,CH_4} p_{gas,CH4}) \tag{5.4b}$$

$$\rho_{T,IC} = k_L a(S_{liq,CO_2} - K_{H,CO_2} p_{gas,CO2}) \tag{5.4c}$$

where $\rho_{T,i}$ is the transfer rate of gas i and $S_{liq,CO2}$ is the fraction of inorganic carbon as CO_2. This is shown in matrix format in Appendix B.

5.2 GAS PHASE EQUATIONS

The gas phase rate equations are very similar to the liquid phase equations, except there is no advective influent flow, and only dynamic state components. The dynamic states can be either in pressure (bar), or concentration (M or kgCOD m^{-3}). During testing, we used gas concentration, with pressure calculated from concentration based on the ideal gas law p = SRT, where S is the concentration in M. The differential equations for the gas phase with a constant gas volume (from Eq. (5.2)) are:

$$\frac{dS_{gas,i}}{dt} = -\frac{S_{gas,i} q_{gas}}{V_{gas}} + \rho_{T,i} \frac{V_{liq}}{V_{gas}} \tag{5.5}$$

The term V_{liq}/V_{gas} is required as the gas transfer kinetic rate is liquid volume-specific. The pressure of each gas component can be calculated using the ideal gas law for the three gases (in bar, factors in denominators are COD equivalents of the gases):

$$p_{gas,H_2} = S_{gas,H_2} RT/16 \tag{5.6a}$$

$$p_{gas,CH_4} = S_{gas,CH_4} RT/64 \tag{5.6b}$$

$$p_{gas,CO_2} = S_{gas,CO_2} RT \tag{5.6c}$$

The reactor headspace can be assumed to be water vapour saturated. Temperature dependence of water vapour pressure is well described by Eq. (4.10). Substituting a water vapour pressure of 0.0313 bar at 298 K and ΔH^0_{vap} of 43,980 J mole^{-1} (Lide 2001) into Eq. (4.10) results in Eq. (5.7):

$$p_{gas,H_2O} = 0.0313 \exp\left(5290\left(\frac{1}{298} - \frac{1}{T}\right)\right) \tag{5.7}$$

where T is the temperature in K. The most common way to calculate the gas flow is to set it equal to total gas transfer, corrected for water vapour (Eq. (5.8)).

$$q_{gas} = \frac{RT}{P_{gas} - p_{gas,H_2O}} V_{liq}\left(\frac{\rho_{T,H2}}{16} + \frac{\rho_{T,CH4}}{64} + \rho_{T,CO2}\right) \tag{5.8}$$

where P_{gas} is the set headspace total pressure (normally 1.013 bar). If the headspace pressure is variable, or there is downstream processing of the gas, the gas flow can be calculated by a control loop in pressure. To do this, the gas phase pressure must be calculated from partial pressures (Eq. (5.9)), and the flow calculated for restricted flow through an orifice.

$$P_{gas} = p_{gas,H_2} + p_{gas,CH_4} + p_{gas,CO_2} + p_{gas,H_2O} \tag{5.9}$$

$$q_{gas} = k_p\,(P_{gas} - P_{atm}) \tag{5.10}$$

where k_P is the pipe resistance coefficient (m^3 d^{-1} bar^{-1}) and P_{atm} is the external (atmospheric) pressure. This function also has an advantage in tall reactors, where the gas pressure due to hydraulics may be significantly higher than in laboratory reactors.

5.3 SPECIFIC EXAMPLE: INORGANIC CARBON

This is an example of implementation of the inorganic carbon states in liquid and gas phases for both DAE and DE formulation. Further details for physico-chemical reactions are given in Appendix B.

5.3.1 DAE system

Substituting the inorganic carbon (S_{IC}) into Eq. (5.2) gives the liquid mass balance:

$$\frac{dS_{liq,IC}}{dt} = \frac{q_{in}S_{in,IC}}{V_{liq}} - \frac{q_{out}S_{liq,IC}}{V_{liq}} + \sum_{j=1-19}\rho_j\nu_{10,j} - \rho_{T,CO2} \tag{5.11}$$

where $S_{liq,10} \equiv S_{liq,IC}$. In addition, the free and ionic fractions of S_{IC} (S_{CO2} and S_{HCO3} respectively) are calculated as part of the algebraic set of equations (from Eqs (4.3) and (4.4)):

$$S_{IC} - S_{CO_2} - S_{HCO_3^-} = 0 \tag{5.12}$$

$$S_{HCO_3^-} - \frac{K_{a,CO_2} S_{IC}}{K_{a,CO_2} + S_{H^+}} = 0 \tag{5.13}$$

where $K_{a,CO2}$ is the acid-base equilibrium coefficient. The gas phase equations are as shown in Section 5.2. All S_i variables except S_{IC} are algebraic.

5.3.2 DE system

When the inorganic carbon system is implemented as a DE system, the variables S_{CO2} and S_{HCO3} are dynamic and S_{IC} is not used. The two dynamic equations for S_{CO2} and S_{HCO3} respectively are:

$$\frac{dS_{liq,CO_2}}{dt} = \frac{q_{in} S_{in,CO_2}}{V_{liq}} - \frac{q_{out} S_{liq,CO_2}}{V_{liq}} + \sum_{j=1-19} \rho_j \nu_{10,j} - \rho_{T,CO2} + \rho_{A/BCO2} \tag{5.14}$$

and

$$\frac{dS_{liq,HCO_3^-}}{dt} = -\frac{q_{out} S_{liq,HCO_3^-}}{V_{liq}} - \rho_{A/BCO2} \tag{5.15}$$

where $S_{liq,10} \equiv S_{liq,CO2}$. There is also an additional rate equation for acid-base reactions:

$$\rho_{A/BCO2} = k_{A/BCO2}\left(S_{liq,HCO3} S_{liq,H+} - K_{a,CO2} S_{liq,CO2}\right) \tag{5.16}$$

where $\rho_{A/BCO2}$ ($M\ d^{-1}$) is the production rate of CO_2 from HCO_3 (i.e. base to acid, $M\ d^{-1}$), $k_{A/BCO2}$ ($M^{-1}\ d^{-1}$) is the dynamic parameter, which should be set to only one order of magnitude higher than the highest biochemical rate (after adjustment of units) to reduce model stiffness and $K_{a,CO2}$ is the CO_2/HCO_3^- equilibrium coefficient (M). If all acids and bases are implemented in this manner, and the hydroxide ion equilibrium equation (Eq. (4.7)) substituted into the charge balance (Eq. (4.2)), the only algebraic equation is the charge balance and there is an explicit solution for S_{H+}.

6

Suggested biochemical parameter values, sensitivity and estimation

The key criticism of structured models is that, because of their complexity, there is a large number of parameters. Fortunately, the kinetic parameters are generally less variable than in activated sludge systems, and parameter values from a variety of applications are given in Appendix A. Some suggested stoichiometric coefficients are given in Table 6.1. Suggested kinetic parameter values for mesophilic high-rate, mesophilic solids, and thermophilic solids digesters as well as qualitative variation and sensitivity are given in Table 6.2. These parameters have been tested on data sets for consistency, and will give reasonable prediction of system response under a number of conditions, but are largely arbitrary, based on our experience. For more application-specific values, see Appendix A. Physico-chemical parameters are given in Chapter 4, and (with the exception of k_La) are independent of application.

Methods for biochemical parameter estimation for anaerobic models is one of the areas in which the literature is less developed, and we believe that a number of valuable contributions can be made to facilitate systematic and repeatable parameter estimation and, just as importantly, parameter sensitivity and identifiability. Associated with this, we found numerical methods for parameter optimisation and parameter identifiability to be very valuable during internal testing and analysis of systems (in particular, the Simplex method (Nelder and Mead 1965) was used extensively for parameter optimisation). Our strategy for parameter estimation was generally to minimise the number of biochemical parameters to be optimised numerically by: (a) taking those with a low variability, such as K_I, and Y, from literature values; (b) taking more variable parameters from studies with similar reactor design and feed matrix (if available); and (c) reducing parameters by numerical analysis of

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sensitivity, correlation and identifiability. This reduction process generally resulted in requiring numerical estimation of one or two parameters each for the acetogenic and aceticlastic biological groups, or hydrolysis for optimal prediction. Reasonable prediction of all variables was in most cases achieved by steps (a) or (b) listed above. Parameters requiring numerical optimisation were generally those listed in Table 6.2, which have both a high variability and cause significant changes in model outputs. These are addressed further below.

Table 6.1: Suggested stoichiometric parameters and qualitative sensitivity and variability.

Parameter (dimensionless)	Description	Value	Var	Notes
$f_{sI,xc}$	Soluble inerts from composites	0.1	2	1
$f_{xI,xc}$	Particulate inerts from composites	0.25	2	1
$f_{ch,xc}$	Carbohydrates from composites	0.20	2	1
$f_{pr,xc}$	Proteins from composites	0.20	2	1
$f_{li,xc}$	Lipids from composites	0.25	2	1
N_{xc}, N_I	Nitrogen content of composites and inerts	0.002	2	1
$f_{fa,li}$	Fatty acids from lipids	0.95	1	2
$f_{h2,su}$	Hydrogen from sugars	0.19	3	3
$f_{bu,su}$	Butyrate from sugars	0.13	3	3
$f_{pro,su}$	Propionate from sugars	0.27	3	3
$f_{ac,su}$	Acetate from sugars	0.41	3	3
$f_{h2,aa}$	Hydrogen from amino acids	0.06	2	3
N_{aa}	nitrogen in amino acids and proteins	0.007	2	3
$f_{va,aa}$	Valerate from amino acids	0.23	2	3
$f_{bu,aa}$	Butyrate from amino acids	0.26	2	3
$f_{pro,aa}$	Propionate from amino acids	0.05	2	3
$f_{ac,aa}$	Acetate from amino acids	0.40	2	3

Var = variability of parameter. 1 = varies very little between processes; 2 = varies between processes and substrates; 3 = varies dynamically within process.

1. Varies widely; see Gossett and Belser (1982) to estimate inerts in activated sludge.
2. Based here on palmitate triglyceride. Varies between 91–98% depending on LCFA chain length.
3. See Appendix D to estimate products from sugars and amino acids.

6.1 HYDROLYSIS PARAMETERS

In many cases there are one or two significant parameters. In solids digesters fed with a relatively homogeneous substrate such as primary or activated sludge, the important kinetic parameter is disintegration of composites, as subsequent hydrolysis is commonly much faster. The most important stoichiometric parameter is the inert fraction (Pavlostathis and Gossett 1986). To estimate fractions of inerts (1–D) and first-order disintegration parameters, Pavlostathis and Gossett (1986) and Gossett and Belser (1982) are recommended.

In systems fed with a heterogeneous mixture of particulate protein and lipids or carbohydrates the influent matrix would reflect this, and the important parameters are protein and lipid or carbohydrate hydrolysis. In this case, the disintegration process is only used for recycling of decayed biomass, which is a relatively small fraction of the COD flux. Fitting of parameters in these systems is assisted, as the feed normally contains either protein and lipids (mainly animal or food-processing), or carbohydrate particulates (carbohydrate food processing, brewery, starch, etc.).

Table 6.2: Suggested parameter values and qualitative sensitivity and variability.

Parameter	Mesophilic high-rate (nom 35°C)	Mesophilic solids (nom 35°C)	Thermophilic solids (nom 55°C)	S	Var	Notes
k_{dis} (d^{-1})	0.4	0.5	1.0	3	3	1
k_{hyd_CH} (d^{-1})	0.25	10	10	3	2	2
k_{hyd_PR} (d^{-1})	0.2	10	10	3	2	2
k_{hyd_LI} (d^{-1})	0.1	10	10	2	3	2
$t_{res,X}$ (d)	40	0	0	3	2	
k_{dec_all} (d^{-1})	0.02	0.02	0.04	2	2	3
$K_{S\_NH3\_all}$ (M)	1×10^{-4}	1×10^{-4}	1×10^{-4}	1	1	
$pH_{UL\ acet/acid}$	5.5	5.5	5.5	1	2	4
$pH_{LL\ acet/acid}$	4	4	4	1	2	4
k_{m_su} (COD COD^{-1} d^{-1})	30	30	70	1	2	
K_{S_su} (kgCOD m^{-3})	0.5	0.5	1	1	2	
Y_{su} (COD COD^{-1})	0.10	0.10	0.10	1	1	
k_{m_aa} (COD COD^{-1} d^{-1})	50	50	70	1	2	
K_{S_aa} (kgCOD m^{-3})	0.3	0.3	0.3	1	1	
Y_{aa} (COD COD^{-1})	0.08	0.08	0.08	1	1	
k_{m_fa} (COD COD^{-1} d^{-1})	6	6	10	1	3	
K_{S_fa} (kgCOD m^{-3})	0.4	0.4	0.4	1	3	
Y_{fa} (COD COD^{-1})	0.06	0.06	0.06	1	1	
$K_{I,H2\_fa}$(kgCOD m^{-3})	$5 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	n/a	1	1	
k_{m_c4+} (COD COD^{-1} d^{-1})	20	20	30	1	2	
K_{S_c4+} (kgCOD m^{-3})	0.3	0.2	0.4	1	3	
Y_{c4+}(COD COD^{-1})	0.06	0.06	0.06	1	1	
$K_{I,H2\_c4+}$(kgCOD m^{-3})	1×10^{-5}	1×10^{-5}	3×10^{-5}	1	1	
k_{m_pro} (COD COD^{-1} d^{-1})	13	13	20	2	2	
K_{S_pro} (kgCOD m^{-3})	0.3	0.1	0.3	2	2	
Y_{pro} (COD COD^{-1})	0.04	0.04	0.05	1	1	
$K_{I,H2\_pro}$(kgCOD m^{-3})	3.5×10^{-6}	3.5×10^{-6}	1×10^{-5}	2	1	
k_{m_ac} (COD COD^{-1} d^{-1})	8	8	16	3	2	
K_{S_ac} (kgCOD m^{-3})	0.15	0.15	0.3	3	2	
Y_{ac} (COD COD^{-1})	0.05	0.05	0.05	1	1	
$pH_{UL\ ac}$	7	7	7	3	1	5
$pH_{LL\ ac}$	6	6	6	2	1	5
$K_{I,NH3}$ (M)	0.0018	0.0018	0.011	2	1	
k_{m_h2} (COD COD^{-1} d^{-1})	35	35	35	1	2	
K_{S_h2} (kgCOD m^{-3})	2.5×10^{-5}	7×10^{-6}	5×10^{-5}	2	2	
Y_{h2} (COD COD^{-1})	0.06	0.06	0.06	1	1	
pH_{UL_h2}	6	6	6	2	2	5
pH_{LL_h2}	5	5	5	1	1	5

S = sensitivity of important output to parameter at average parameter values. 1 = low or no sensitivity of all outputs to parameter; 2 = some sensitivity or significant sensitivity under dynamic conditions; 3 = significant sensitivity under steady-state conditions and critical sensitivity under dynamic conditions.

Var = variability of parameter. 1 = varies within 30%; 2 = varies within factor of 100%; 3 = varies within factor of 300%.

1. Mainly of importance in solids digesters.
2. Mainly of importance for pure or semi-separated solid substrates (such as slaughterhouse or starch). When used with activated sludge digesters, k_{dis} is rate-limiting.
3. Decay rates can be set equal as a first guess. In many cases, a k_{dec} double the given values can be used for certain groups, such as acidogens and aceticlastic methanogens.
4. $pH_{acet/acid}$ inhibition factors for all acidogenic and acetogenic bacteria. Form 2 is used here (i.e. only low pH inhibition).
5. Notes as for (4), except values are methanogen-specific.

6.1.1 Parameters associated with propionate

The key parameters in order of variability are $K_{S\_pro,}$ k_{m_pro} and k_{decay}, which can generally be fitted by either a number of steady-state conditions, or a single dynamic experiment. Under higher loading conditions, hydrogen inhibition becomes important.

6.1.2 Parameters associated with acetate

The critical parameters here are again $K_{S,ac}$ and $k_{m,ac}$, which can normally be estimated as for propionate under medium and low loading conditions. pH inhibition can also have an effect on fitting of the above parameters. We have also observed some variation of the decay rate for aceticlastic methanogens between solids digesters and high-rate systems, with the decay increasing in solids digesters. $K_{I,NH3,ac}$ is also very important in systems with high ammonia concentrations, but there is often a low variability in this parameter between systems in continuous reactors (Siegrist and Batstone 2001).

7
Conclusion

Over the last 30 years there has been an increasing level of understanding of anaerobic processes and application of structured anaerobic digestion models. Our job as a task group has been to consolidate this work, and increase its accessibility to researchers and practitioners at a broad level. As such, three main areas have been addressed:

(1) unified nomenclature, units and kinetics;
(2) biochemical reaction structure, and kinetics; and
(3) physico-chemical reaction structure.

To increase the utility of the ADM1, we also addressed implementation in a continuous-flow stirred-tank reactor (CSTR) system, which is the simplest and most commonly encountered application. This chapter should assist in the use of the model but does not form an integral part of it. The key elements of the ADM1, listed as (1)–(3) above, are largely independent of the type of application. As such, this model should be applicable in a number of other systems such as solid phase digesters, plug flow reactors and biofilm reactors.

There are two broad fields for application of the ADM1. Researchers and practitioners can use it as presented here for design, analysis and optimisation of existing and theoretical processes. One of the main considerations in the development of nomenclature, units and structure has been integration with existing standards and, in particular, the activated sludge models ASM1–3. Exchange of state variables between the ADM1 and ASM-based models is relatively simple. The suggested parameter set should also assist application, as it allows good prediction of COD and mass balancing (i.e. gas flow, composition and effluent COD), and reasonable prediction of secondary variables such as organic acids and pH with a variety of feed and reactor types. The second application of the ADM1 is as a base for further model

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development and modification. Both the biochemical and physico-chemical equation structures are highly expandable, and using the ADM1 as a basis will allow more consistent and easier presentation and application of future modifications and add-ons.

During formulation of the ADM1, the task group considered a number of processes that were not included in the model, either because they were not encountered often enough to warrant inclusion in a broad-based model or, in many cases, because of limited available information in the literature. Special boxes referring to processes omitted from the ADM1 have been placed throughout the report. These limitations are briefly summarised in Table 7.1, and are worthwhile subjects for extensions of the base model.

Table 7.1: Processes omitted from ADM1 and addressed in boxes.

Process omitted	Part of ADM1 affected
Glucose alternative products	Biochemical structure: regulation of products from acidogenesis of glucose and alternatives such as lactate and ethanol
Sulfate reduction and sulfide inhibition	Biochemical, physico-chemical structure and kinetics when sulfate present in feed
Nitrate	Biochemical structure: mainly electron flow or channelling; competition for electron donor and/or electron acceptor
Weak acid and base inhibition	Inhibition kinetics: mainly methanogens
LCFA inhibition	Inhibition kinetics: mainly methanogens
Acetate oxidation	Biochemical structure: additional group may compete with aceticlastic methanogens to produce hydrogen at high temperatures
Homoacetogenesis	Biochemical structure: additional group may compete with hydrogen utilising methanogens to produce acetate at low temperatures
Solids precipitation	Physico-chemical structure: Inorganic carbon, inorganic nitrogen and metallic ions precipitate to solids

The task group also identified a number of areas where the available information is limited or completely lacking. These potentially valuable areas of research include:

- detailed effects of a number of inhibitory compounds on the various biochemical processes;
- changes in population characteristics and kinetics across the temperature ranges of psychrophilic, mesophilic and thermophilic operation;
- methods for biological parameter identification, measurement and error analysis; and
- analysis and validation of existing and future parameters with a variety of feed types and reactor design.

In conclusion, we hope that this model will be of service to the community of engineers and scientists working in anaerobic digestion and degradation processes, and that it will promote further application and research in this growing and fascinating field.

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Appendix A: Review of parameters

Table A.1: Disintegration and hydrolytic parameters.

Ref.	k_{dis} (d^{-1})	k_{hyd_CH} (d^{-1})	k_{hyd_PR} (d^{-1})	k_{hyd_LI} (d^{-1})	Determination	Substrate	pH	Temp. (°C)
1	0.24	1.0	1.0		dynamic	manure/oil	8	55
2			0.29	0.12	dynamic	slaughterhouse	6–7	33
3			0.2		batch	primary sludge	7	35
4		0.30	0.28		steady state	primary sludge	5.14	35
4		0.41	0.39		steady state	primary sludge	5.85	35
4		0.58	0.58		steady state	primary sludge	6.67	35
5		0.28	0.68		batch	piggery	7±0.03	35
5		0.19	0.35		batch	olive-mill	7±0.03	35
5		0.13	0.24		batch	dairy	7±0.03	35
6		106			batch	lactose	7±0.03	35
6			2.7		batch	gelatin	7±0.03	35
7 (max)		0.13	0.03	0.08	lit. rev.	various		34–40
7 (min)		0.041	0.020	0.40	lit. rev.	various		34–40
8	0.54				regression	forest soil		30
8	0.09–0.31				regression	forest soil		20
8	0.054–0.075				regression	forest soil		15
8	0.013				dynamic	pond silt		28
8	0.0041				dynamic	pond silt		15
8			0.12		dynamic	proteins		28
10 (max)		1.94	0.10	0.17	steady state	primary sludge		35
10 (min)		0.21	0.0096	0.0096	steady state	primary sludge		35
11			0.1–0.15		batch	fish waste	4–8	33
15	0.70				dynamic	slaughterhouse		35

Table A.1: Disintegration and hydrolytic parameters (continued).

Ref.	k_{dis} (d^{-1})	k_{hyd_CH} (d^{-1})	k_{hyd_PR} (d^{-1})	k_{hyd_LI} (d^{-1})	Determination	Substrate	pH	Temp. (°C)
16	0.25				dynamic	primary sludge	7.2–7.7	35
16	0.4				dynamic	primary sludge	7.2–7.7	55
18		0.150			dynamic	cellulose		28
20	0.096				dynamic	pig manure		28
20	0.13				dynamic	cattle manure		6
21	0.41				dynamic	food waste		37

Table A.2: Kinetic parameters for monosaccharide acidogenesis.

Ref.	K_m (COD COD^{-1} d^{-1})	K_s (kgCOD m^{-3})	Y (COD COD^{-1})	K_{dec} (d^{-1})	μ_{max} (d^{-1})	Determination	Substrate	Temp. (°C)	pH_{ul}	pH_{ll}	pH form
1	49.3	0.533	0.10	0.01	5.1	dynamic	manure/oil	55			
7	51	0.022	0.14		7.20	lit. rev.	glucose	30			
12 (max)	125	0.630	0.17		21.25	lit. rev.	glucose	35–37			
12 (min)	29	0.023	0.01		0.41						
14	120	1.280	0.07	0.02	8.78	dynamic	molasses	35	5.5	4	lower only
16	27	0.050	0.15	0.80	4.00	dynamic	primary sludge	35	5.5	4.5	lower only
16	107	0.200	0.15	3.20	16.00	dynamic	primary sludge	55	5.5	4.5	lower only
17	5067	0.049				batch	glucose	35			

Table A.3: Kinetic parameters for amino acid acidogenesis.

Ref.	k_m (COD COD^{-1} d^{-1})	K_s (kgCOD m^{-3})	Y (COD COD^{-1})	k_{dec} (d^{-1})	μ_{max} (d^{-1})	Determination	Substrate	Temp. (°C)	pH_{ul}	pH_{ll}	pH form
1	74		0.086	0.010	6.38	dynamic	manure/oil	55			
13	36	1.198	0.085	0.020	3.06	dynamic	casein	35	5.5	4	lower only
13	28	1.027	0.085	0.020	2.36	dynamic	casein	35	5.5	4	lower only
13	53	1.198	0.058	0.020	3.05	dynamic	casein	35	7.2	5	lower only
16	27	0.050	0.15	0.80	4.00	dynamic	primary sludge	35	5.5	4.5	lower only
16	107	0.200	0.15	3.20	16.00	dynamic	primary sludge	55	5.5	4.5	lower only

Table A.4: Kinetic parameters for LCFA acetogenesis.

Ref.	k_m (COD COD^{-1} d^{-1})	K_s (kgCOD m^{-3})	Y (COD COD^{-1})	k_{dec} (d^{-1})	μ_{max} (d^{-1})	Determination	Substrate	Temp. (°C)	pH_{ul}	pH_{ll}	pH form
1	11	0.058	0.050	0.010	0.55	dynamic	oleate/manure/oil	55	8.5	6	upper/lower
9	1.88	0.295	0.055	0.010	0.10	steady state	stearate	37			
9	2.030	0.41	0.054	0.010	0.11	steady state	palmitate	37			
9	1.60	1.23	0.053	0.010	0.08	steady state	myristate	37			
9	8.174	9.21	0.054	0.010	0.44	steady state	oleate	37			
9	10.0	5.19	0.055	0.010	0.55	steady state	linoleate	37			
15	363	0.10	0.021		7.70	dynamic	slaughterhouse (stearate)	35			
15	201	0.10	0.004		0.89	dynamic	slaughterhouse (palmitate)	35			
16[a]	12	1.00	0.05	0.06	0.55	dynamic	primary sludge	35	6.7	5.8	lower only
16[b]	37	2.00	0.05	0.20	1.65	dynamic	primary sludge	55	6.7	5.8	lower only

Notes: (a) $K_{I,H2} = 3 \times 10^{-6}$ kgCOD m^{-3}, $K_{I,ac} = 1.5$ kgCOD m^{-3} (b) $K_{I,H2} = 15 \times 10^{-6}$ kgCOD m^{-3}, $K_{I,ac} = 1.5$ kgCOD m^{-3}

Table A.5: Kinetic parameters for valerate acetogenesis.

Ref.	k_m (COD COD^{-1} d^{-1})	K_s (kgCOD m^{-3})	Y (COD COD^{-1})	k_{dec} (d^{-1})	μ_{max} (d^{-1})	Determination	Substrate	Temp. (°C)	pH_{ul}	pH_{ll}	pH form
1[a]	13.7	0.357	0.050	0.010	0.69	dynamic	manure/oil	55	8.5	6	upper and lower
13[b]	22	0.062	0.055	0.030	1.20	dynamic	casein	35	6	4	lower only

Notes: (a) $K_{I,ac}$ = 0.43 kgCOD m^{-3} (b) $K_{I,H2} = 8 \times 10^{-6}$ kgCOD m^{-3}

Table A.6: Kinetic parameters for butyrate acetogenesis.

Ref.	k_m (COD COD^{-1} d^{-1})	K_s (kgCOD m^{-3})	Y (COD COD^{-1})	k_{dec} (d^{-1})	μ_{max} (d^{-1})	Determination	Substrate	Temp. (°C)	pH_{ul}	pH_{ll}	pH form
1[a]	8.4	0.318	0.079	0.010	0.67	dynamic	manure/oil	55	8.5	6	upper and lower
7	5.6	0.013	0.066	0.027	0.37	lit. rev.	butyrate	35			
12 (max)	14	0.298	0.066	0.027	0.89	lit. rev.	butyrate	35–60			
12 (min)	5.3	0.012	0.066	0.027	0.35	lit. rev.					
13[b]	32	0.080	0.066	0.030	2.08	dynamic	casein	35	6	4	lower only
14[b]	41	0.280	0.066	0.030	2.70	dynamic	molasses	35	6	4	lower only
19	89	0.450	0.026	0.30	2.27	dynamic	Ac:Pr:But 25:35:40	55			
19	8.9	0.030	0.026	0.10	0.23	dynamic	Ac:Pr:But 25:35:40	55			

Notes: (a) $K_{I,ac}$ = 1.09 kgCOD m^{-3} (b) $K_{I,H2} = 8 \times 10^{-6}$ kgCOD m^{-3}

Table A.7: Kinetic parameters for propionate acetogenesis.

Ref.	k_m (COD COD^{-1} d^{-1})	K_s (kgCOD m^{-3})	Y (COD COD^{-1})	k_{dec} (d^{-1})	μ_{max} (d^{-1})	Determination	Substrate	Temp. (°C)	pH_{ul}	pH_{ll}	pH form
1[a]	5.5	0.392	0.089	0.010	0.49	dynamic	manure/oil	55	8.5	6	upper/lower
7 (max)	0.31	1.146	0.050	0.041	0.02	lit. rev.	propionate	25–35			
7 (min)	0.16	0.060	0.025	0.010	0.00	lit. rev.					
13[b]	20	0.056	0.055	0.010	1.07	dynamic	casein	35	5.5	4	lower only
14[b]	15	0.373	0.055	0.010	0.80	dynamic	molasses	35	5.5	4	lower only
16[c]	11	0.020	0.05	0.06	0.55	dynamic	primary sludge	35	6.7	5.8	lower only
16[d]	33	0.150	0.05	0.20	1.65	dynamic	primary sludge	55	6.7	5.8	lower only
17	19	0.021				batch	glucose	35			
19[e]	23	0.151	0.019		0.44	dynamic	propionate	37			
19[f]	141	0.300	0.019	0.199	2.68	dynamic	Ac:Pr:But 25:35:40	55			
19[g]	53	0.030	0.019	0.010	1.00	dynamic	Ac:Pr:But 25:35:40	55			

Notes: (a) $K_{I,ac}$ = 1.75 kgCOD m^{-3} (b) $K_{I,H2}$ = 8 × 10^{-6} kgCOD m^{-3} (c) $K_{I,H2}$ = 1 × 10^{-6} kgCOD m^{-3}, $K_{I,ac}$ = 1.5 kgCOD m^{-3}, $K_{I,nh3}$ = 0.002 M (d) $K_{I,H2}$ = 5 × 10^{-6} kgCOD m^{-3}, $K_{I,ac}$ = 1.5 kgCOD m^{-3}, $K_{I,nh3}$ = 0.006 M (e) $K_{I,ac}$ = 2.154 kgCOD m^{-3} (f) $K_{I,ac}$ = 0.65 kgCOD m^{-3} (g) $K_{I,ac}$ = 1 kgCOD m^{-3}

Table A.8: Kinetic parameters for aceticlastic methanogenesis.

Ref.	k_m (COD COD^{-1} d^{-1})	K_s (kgCOD m^{-3})	Y (COD COD^{-1})	k_{dec} (d^{-1})	μ_{max} (d^{-1})	Determination	Substrate	Temp. (°C)	pH_{ul}	pH_{ll}	pH form
1	10.9	0.128	0.055	0.010	0.6	dynamic	manure/oil	55	8.5	6	upper/lower
7 (max)	6.2	0.930	0.076	0.036	0.474	lit. rev.	acetate	25–35			
7 (min)	3.1	0.028	0.032	0.012	0.100	lit. rev.	acetate	25–35			
8	2.7	0.053	0.075		0.199	regression	H_2/CO_2	20			
8	0.3	0.053	0.075		0.020	regression	H_2/CO_2				
12 (max)	19	0.930	0.076	0.004	1.406	lit. rev.	acetate	25–37			
12 (min)	3.4	0.011	0.014	0.036	0.047	lit. rev.	acetate	25–37			
13	8.4	0.096	0.048	0.020	0.401	dynamic	casein	35	7	6	lower only
14	9.4	0.384	0.048	0.020	0.450	dynamic	molasses	35	7	6	lower only
16[a]	13	0.040	0.03	0.05	0.33	dynamic	primary sludge	35	6.7	5.8	lower only
16[b]	52	0.300	0.03	0.20	1.30	dynamic	primary sludge	55	6.7	5.8	lower only
17	48	0.034									
18	6.4	0.035	0.063	0.02	0.41	dynamic	glucose				
19	19	0.107	0.027		0.509	dynamic	propionate	37			
19	21	0.300	0.028		0.591	dynamic	Ac:Pr:Bu 25:35:40	55			
19	8.8	0.030	0.028	0.010	0.247	dynamic	Ac:Pr:Bu 25:35:40	55			
19	7.9	0.213	0.038		0.298	steady state	Acetate	37			
20	0.14–8.0	0.028	0.025	0.010		dynamic	H_2/CO_2	6–28			

Notes: (a) $K_{I,nh3}$ = 0.0012 M (b) $K_{I,nh3}$ = 0.0068 M

Table A.9: Kinetic parameters for hydrogen-utilising methanogenesis.

Ref.	k_m (COD COD^{-1} d^{-1})	K_s (kgCOD m^{-3})	Y (COD COD^{-1})	k_{dec} (d^{-1})	μ_{max} (d^{-1})	Determination	Substrate	Temp. (°C)	pH_{ul}	pH_{ll}	pH form
7	25	6.0E–04	0.056		1.4	pure culture		33			
12 (max)	64	6.0E–04	0.183	0.009	12	lit. rev.	H_2/butyrate	33-60			
12 (min)	1.68	1.8E–05	0.014		0.02						
14	43	8.8E–05	0.060	0.009	2.6	dynamic	molasses	35	6	5	lower only
16	44	1.0E–06	0.05	0.30	2.0	dynamic	primary sludge	35	6.7	5.8	lower only
16	178	5.0E–06	0.05	1.20	8.0	dynamic	primary sludge	55	6.7	5.8	lower only

References cited throughout Appendix A:

1. Angelidaki *et al*. (1999); 2. Batstone (2000); 3. Boon (1994); 4. Eastman and Ferguson (1981); 5. Gavala *et al*. (1999); 6. Gavala and Lyberatos (2001); 7. Gujer and Zehnder (1983); 8. Lokshina and Vavilin (1999); 9. Novak and Carlson (1970); 10. O'Rourke (1968); 11. Palenzuella Rollon (1999); 12. Pavlostathis and Giraldo-Gomez (1991); 13. Ramsay (1997); 14. Romli *et al*. (1995); 15. Salminen *et al*. (2000); 16. Siegrist *et al*. (2002); 17. Skiadas *et al*. (2000); 18. Stamatelatou (1999); 19. Vavilin *et al*. (1996); 20. Vavilin *et al*. (1997); 21. Vavilin *et al*. (1998); 22. Vavilin *et al*. (1999).

Appendix B: Supplementary matrix information

This appendix presents additional information that supplements the kinetic biochemical reaction rate equations and stoichiometric coefficients given in Tables 3.1 and 3.2. This includes a basic description of the matrix method of model presentation, and detailed equations describing physico-chemical processes.

B.1 MODEL PRESENTATION IN MATRIX FORMAT

The main purpose of this section is to summarise the matrix model presentation method for those not familiar with the Activated Sludge Models (ASM) models, where it is used widely. Much of this section is summarised from Henze *et al.* (1987), which contains a more detailed explanation.

For each component, the mass balance within a system boundary can be expressed as follows:

$$\text{Accumulation} = \text{Input} - \text{Output} + \text{Reaction} \tag{B.1}$$

The input and output terms describe mass flow across the system boundaries, and depend on the physical characteristics of the system modelled. Within the reaction term, there are a number of specific processes (such as growth, hydrolysis, decay, etc.) that also influence other components. The matrix method represents the reaction terms for each component, subdivided by processes. Moving vertically through the matrix the process index (j) changes; while moving horizontally, the component index (i) changes. The process index and description is given in the left hand column, while the component index and nomenclature is

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given in the topmost row. In the right-hand column the process rate (ρ_j) for each process is given, while the remainder of each row is filled with the stoichiometric coefficients ($\nu_{i,j}$) that describe the influence of that row's process on individual components. The overall volume-specific reaction term (r_i) for each component i can be formulated by summing the products of the stoichiometric coefficients in column i and process rates:

$$r_i = \sum_j \nu_{i,j}\rho_j \tag{B.2}$$

For example, the overall rate of reaction for monosaccharides (r_1) is:

$$r_1 = \sum_j \nu_{i,j}\rho_j = k_{hyd,ch}X_{ch} + (1 - f_{fa,li})k_{hyd,li}X_{li} - k_{m,su}\frac{S_{su}}{K_S + S}X_{su}I_1 \tag{B.3}$$

Hydrolysis of carbohydrates

Hydrolysis of lipids

Uptake of sugars

As such, the matrix only identifies the reaction terms, and the physical configuration also needs definition to complete the model. Methods for doing this in a continuous-flow stirred-tank reactor configuration are demonstrated in Chapter 5.

Another advantage of the matrix presentation method is that the conservation of COD, nitrogen, and carbon (continuity) can be easily checked. The stoichiometric coefficients (after adjustment to consistent units) for each row should add up to zero, as COD, carbon or nitrogen lost from reactants must flow to products. This can be easily checked in a spreadsheet before implementing in a specific system configuration, which will reveal most stoichiometric errors in COD, carbon and nitrogen balancing. COD is the basis of the matrix, and COD conservation can be calculated by placing the matrix in a spreadsheet and substituting (or linking) f and Y values. The non-COD components (S_{IC}, S_{IN}) should be omitted from the row-wise COD conservation calculation. Carbon and nitrogen conservation can be checked by multiplying column-wise by C_i and N_i respectively, and recalculating row-wise (making sure to include S_{IC} and S_{IN} for carbon and nitrogen checks respectively). An example conservation calculation for COD, carbon and uptake of sugars (j = 5) is shown in Table B.1 (non-contributing components are omitted; ADM1 default parameters).

Table B.1: COD, carbon and nitrogen conservation test for uptake of sugars (j = 5).

	1	5	6	7	8	10	11	17	Σ
	S_{su}	S_{bu}	S_{pro}	S_{ac}	S_{h2}	S_{IC}	S_{IN}	X_{su}	
COD	–1	0.117	0.243	0.369	0.171	–	–	0.1	0
Carbon	–0.0313	0.0029	0.0065	0.0115	–	0.0072	–	0.0031	0
Nitrogen	–	–	–	–	–	–	–0.00063	0.00063	0

B.2 MATRIX FOR GAS TRANSFER

The matrix shown here in Table B.2 is mainly to assist those familiar with the matrix method of kinetic rate presentation, but not with gas–liquid transfer equations. It is meant to assist comprehension, and should be used in conjunction with Sections 5.1 and 5.2 of the main report. The stoichiometric coefficients for production of gas in the gas phase are not shown, since the kinetic rate equation is liquid volume-specific, and resulting effective coefficients are therefore dependent on reactor configuration and design. Equations for formulating the differential gas phase equations in a fixed volume gas phase are in Section 5.2. Because the

destination of mass conversion is not shown in Table B.2, conservation checks are not possible (or required).

Table B.2: Liquid phase yield coefficients ($\nu_{i,j}$) and rate equations (ρ_j) for liquid–gas reactions.

Component → i		8	9	10	Rate (ρ_j)
j	Process ↓	S_{h2}	S_{ch4}	S_{IC}	
T8	H_2 Transfer	–1			$k_L a(S_{liq,H_2} - 16 K_{H,H_2} p_{gas,H_2})$
T9	CH_4 Transfer		–1		$k_L a(S_{liq,CH_4} - 64 K_{H,CH_4} p_{gas,CH4})$
T10	CO_2 Transfer			–1	$k_L a(S_{liq,CO_2} - K_{H,CO_2} p_{gas,CO_2})$

B.3 IMPLICIT ALGEBRAIC EQUATION SET FOR CALCULATION OF ACID-BASE EQUILIBRIUM IN DAE IMPLEMENTATION

This subsection gives the full implicit algebraic equation set when implementing the ADM1 as a differential-algebraic equation (DAE) set of equations. If implementing as a differential equation (DE) set of equations, see the next subsection.

Table B.3: Acid-base equilibria algebraic equation set.

Equation	Unknown algebraic (arbitrary)
$S_{Cat^+} + S_{NH_4^+} + S_{H^+} - S_{HCO_3^-} - \frac{S_{Ac^-}}{64} - \frac{S_{Pr^-}}{112} - \frac{S_{Bu^-}}{160} - \frac{S_{Va^-}}{208} - S_{OH^-} - S_{An^-} = 0$	S_{H^+}
$S_{OH^-} - \frac{K_w}{S_{H^+}} = 0$	S_{OH-}
$S_{va^-} - \frac{K_{a,va} S_{va,total}}{K_{a,va} + S_{H^+}} = 0$	S_{va^-}
$S_{bu^-} - \frac{K_{a,bu} S_{va,total}}{K_{a,bu} + S_{H^+}} = 0$	S_{bu^-}
$S_{pro^-} - \frac{K_{a,bu} S_{pro,total}}{K_{a,bu} + S_{H^+}} = 0$	S_{pro^-}
$S_{ac^-} - \frac{K_{a,bu} S_{ac,total}}{K_{a,bu} + S_{H^+}} = 0$	S_{ac^-}
$S_{HCO_3^-} - \frac{K_{a,CO_2} S_{IC}}{K_{a,CO_2} + S_{H^+}} = 0$	$S_{HCO_3^-}$
$S_{NH_4^+} - \frac{S_{H^+} S_{IN}}{K_{a,NH_4} + S_{H^+}} = 0$	$S_{NH_4^+}$
$S_{IC} - S_{CO_2} - S_{HCO_3^-} = 0$	S_{CO_2}
$S_{IN} - S_{NH_3} - S_{NH_4^+} = 0$	S_{NH_3}

B.4 MATRIX SUPPLEMENT FOR CALCULATION OF ACID-BASE EQUILIBRIUM IN DE IMPLEMENTATION

This subsection gives the kinetic reaction rates and stoichiometric coefficients for acid-base reactions when implementing the ADM1 as a differential equation (DE) set. For a DE implementation, the free forms S_{hva}, S_{hbu}, S_{hpro}, S_{hac}, S_{co2} and S_{nh3} should be substituted for the total forms S_{va}, S_{bu}, S_{pro}, S_{ac}, S_{IC} and S_{IN} in Tables 3.1, 3.2 and the equations describing gas–liquid transfer. The following equation for calculating hydrogen ion concentration can be used (Eq. (4.7) substituted into Eq. (4.2)):

$$S_{Cat^+} + S_{NH_4^+} + S_{H^+} - S_{HCO_3^-} - \frac{S_{Ac^-}}{64} - \frac{S_{Pr^-}}{112} - \frac{S_{Bu^-}}{160} - \frac{S_{Va^-}}{208} - \frac{K_w}{S_{H^+}} - S_{An^-} = 0 \qquad \text{(B.4)}$$

Table B.4: Rate coefficients ($\nu_{i,j}$) and kinetic rate equations (ρ_j) for acid-base reactions in a DE implementation of the ADM1.

Component → i		4a	4b	5a	5b	6a	6b	7a	7b	10a	10b	11a	11b	Rate (ρ_j, kgCOD m^{-3} d^{-1})
j	**Process ↓**	S_{hva}	S_{va-}	S_{hbu}	S_{bu-}	S_{hpro}	S_{pro-}	S_{hac}	S_{ac-}	S_{co2}	S_{hco3-}	S_{nh4+}	S_{nh3}	
A4	Valerate acid-base	1	–1											$k_{A/Bva}(S_{va^-} S_{H^+} - K_{a,va}S_{hva})$
A5	Butyrate acid-base			1	–1									$k_{A/Bbu}(S_{bu^-} S_{H^+} - K_{a,bu}S_{hbu})$
A6	Propionate acid-base					1	–1							$k_{A/Bpro}(S_{pro^-} S_{H^+} - K_{a,pro}S_{hpro})$
A7	Acetate acid-base							1	–1					$k_{A/Bac}(S_{ac^-} S_{H^+} - K_{a,ac}S_{hac})$
A10	Inorganic carbon acid-base									1	–1			$k_{A/BCO2}(S_{HCO_3^-} S_{H^+} - K_{a,CO2}S_{CO_2})$
A11	Inorganic nitrogen acid-base											1	–1	$k_{A/BIN}(S_{NH_3} S_{H^+} - K_{a,IN}S_{NH_4^+})$
		Valeric acid (kgCOD m^{-3})	Valerate (kgCOD m^{-3})	Butyric acid (kgCOD m^{-3})	Butyrate (kgCOD m^{-3})	Propionic acid (kgCOD m^{-3})	Propionate (kgCOD m^{-3})	Acetic acid (kgCOD m^{-3})	Acetate (kgCOD m^{-3})	Carbon-dioxide (kmoleC m^{-3})	Bicarbonate (kmoleC m^{-3})	Ammonium (kmoleN m^{-3})	Ammonia (kmoleN m^{-3})	*Kinetic parameters*: $k_{A/Bi}$: rate coefficient for the base to acid reaction. May be optimised for each acid-base reaction or initially set to 1×10^8 $M^{-1}d^{-1}$.

Appendix C: Integration with the ASM

This appendix details methods of integration in common or linked models with the ASM series of activated (aerobic) sludge models (Henze *et al.* 1987, 2000).

There are two major differences in implementation of the ADM1, compared to ASMs, excluding structure, states in general and the physico-chemical system:

(1) Units: kgCOD m^{-3} instead of gm^{-3} (mg l^{-1}); M instead of mM for HCO_3^-, M instead of gN m^{-3} (mgN l^{-1}).
(2) Kinetics: are in substrate uptake rather than growth rate.

The reasons for these differences were varied and are covered in detail in the report but can be summarised as: (1) to accommodate the physico-chemical system effectively and in agreement with the majority of anaerobic kinetic studies; and (2) to allow for a better representation of inhibition kinetics when simulating lower yield anaerobic processes.

However, when modelling anaerobic processes together with aerobic processes (either in the same model, linked models or distributed models), it may be desirable to use the same implementation for the ASM and ADM models in order to compare kinetic parameters, and allow use of common states. We recommend use of ASM protocols in these circumstances. There are four major scenarios for implementation of the ASM and ADM1 models together (Figure C.1).

The first three cases can be relatively simply modelled by using the ASMs and ADM1 together. However, the fourth case is more complicated, and is not addressed in this report. Anaerobic polyphosphate release for example, is modelled by the ASM2d (though not as an anaerobic process; Henze *et al.* 2000), and the ASM structure is more appropriate for this process, at least in activated sludge treatment systems. When modelling other special

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processes normally addressed partly by the ASM in anaerobic zones (or vice versa), it is probably better to adapt either the ADM or ASM structure of equations to incorporate those processes, or produce a specialised model.

In the first three cases (the use of ASMs and ADM1 together), the ASMs can be used unmodified, with the ADM1 units modified, or a conversion interface placed between the two models and both models used unmodified. If the first solution is used, it may also be desirable to use the same kinetics as the ASMs in order to directly compare growth rates, and calculate indicators such as safety factors. Modifications of both ADM1 units and kinetics are considered here.

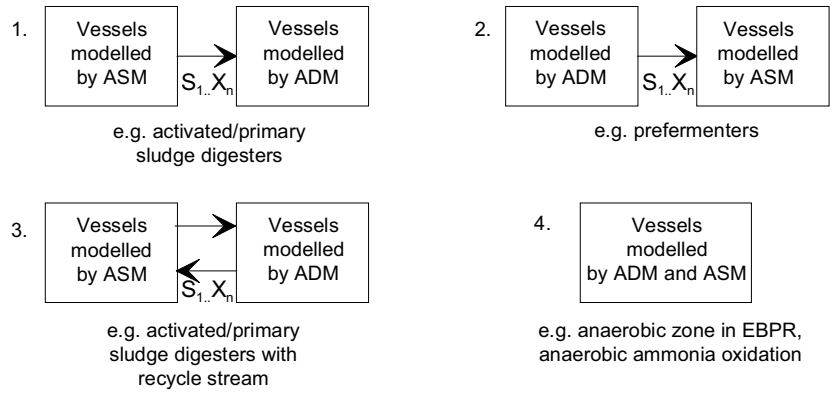

Figure C.1: Scenarios for integration of the ASM and ADM showing outputs from one model ($S_1..X_n$) being used as inputs to the other model. EBPR = enhanced biological phosphorus removal.

C.1 SUBSTITUTING gCOD m^{-3}, mM, AND gN m^{-3} FOR kgCOD m^{-3} AND M

The changes required to parameters are shown in Table C.1.

Table C.1: Changes required converting to ASM units.

Parameter	ADM units	ASM units	Conversion from ADM to ASM
K_S (excluding K_{S_NH3})	kgCOD m^{-3}	gCOD m^{-3}	multiply by 1000
K_{S_NH3}	M	gN m^{-3}	multiply by 14,000
$K_{a,i}$ (excluding $K_{a,w}$)	M	mM	multiply by 1000
$K_{a,w}$	M^2	mM^2	multiply by 1×10^6
K_I (excluding $K_{I,NH3,ac}$)	kgCOD m^{-3}	gCOD m^{-3}	multiply by 1000
$K_{I,NH3,ac}$	M	gN m^{-3}	multiply by 14,000
K_H (excluding $K_{H,CO2}$)	kgCOD m^{-3} bar^{-1}	gCOD m^{-3} bar^{-1}	multiply by 1000
R	bar M^{-1} K^{-1}	bar mM^{-1} K^{-1}	divide by 1000 (8.314×10^{-5})

All dynamic equations can then be expressed in ASM units. Equation (C.1) should be used for the charge balance:

$$S_{Cat^+} + \frac{S_{NH_4^+}}{14} + S_{H^+} - S_{HCO_3^-} - \frac{S_{Ac^-}}{64} - \frac{S_{Pr^-}}{112} - \frac{S_{Bu^-}}{160} - \frac{S_{Va^-}}{208} - S_{OH^-} - S_{An^-} = 0 \qquad (C.1)$$

where the charge balance is expressed in mM, and the acid-base equations in Section 5.3 used as is, since the K_a values have been adjusted for changes in units (it does not matter if a DE or DAE implementation is used). Since the units of S_{H+} have changed to mM, the pH should be calculated as:

$$pH = 3 - \log_{10}(S_{H^+}) \qquad (C.2)$$

All inputs and initial conditions should naturally be in mM, gN m^{-3} and gCOD m^{-3}.

C.2 SUBSTITUTING GROWTH-RELATED (μ_{max}) FOR SUBSTRATE-RELATED (k_m) MONOD KINETICS

The general form for growth-related Monod kinetics is shown in Eq. (C.3)

$$\rho_j = \mu_{max} X \frac{S}{K_S + S} \qquad (C.3)$$

where $\mu_{max} = k_m Y$, and is the maximum specific growth rate. Converting the rate matrices in Tables 3.1 and 3.2 is straightforward and consists of dividing $\nu_{i,j}$ in biochemical uptake rows (j = 5 – 12) by Y_j, where j is the primary substrate, and multiplying process rate $\rho_{i,j}$ by Y_j in the same rows such that $\rho_{i,j,uptake}\, \nu_{i,j,uptake} = \rho_{i,j,growth}\, \nu_{i,j,growth}$. Therefore for processes (rows) j = 5 – 12, the rate coefficients and rates are as follows:

$$\nu_{i,j,growth} = \nu_{i,j,uptake} / Y_j \qquad (C.4)$$

and

$$\rho_{j,growth} = \rho_{j,uptake} \times Y = k_m Y X \frac{S}{K_S + S} \times I_1 \ldots I_n = \mu_{max} X \frac{S}{K_S + S} I_1 \ldots I_n \qquad (C.5)$$

where $I_1 \ldots I_n$ are the secondary substrate, regulation or inhibition functions. Values for μ_{max} can be calculated from $\mu_{max} = k_m Y$, and are also given in Appendix A.

C.3 OUTPUTS FROM ASM SIMULATIONS AS INPUTS IN ADM1

Table C.2: Non-zero outputs from ASM simulations as inputs to the ADM1.

ADM1 name	ADM1 input	Value from ASM outputs
Complex particulates	X_c	$\sum X_i$, excluding X_I
Particulate inerts	X_I	X_I
Soluble inerts	S_I	S_I
Inorganic carbon	S_{IC}	S_{ALK}
Inorganic nitrogen	S_{IN}	S_{NH}
Cations or anions	S_{cat}, S_{an}	None, estimate from measured pH

Note: normally there should be no nitrate/nitrite (S_{NOX}), oxygen (S_{O2}), or RBCOD (S_S) in the feed to an anaerobic digester (nominally from the clarifier underflow). If there is, in the first two cases, an equivalent amount of X_c COD should be removed as there is S_{NOX} and S_{02} in the feed (in terms of COD) (see box on nitrate reduction), while S_S can be nominally added as sugars (S_S).

C.4 OUTPUTS FROM THE ADM AS INPUTS IN ASMS

Table C.3: Non-zero outputs from the ADM1 as inputs to the ASMs.

ASM name	ASM input	Value from ADM outputs
Soluble inerts[1]	S_I	S_I
RBCOD	S_S/S_F	1. $\sum S_i$, excluding S_I, S_{IN} and S_{IC}, if S_A is not used in ASM 2. $\sum S_i$, excluding S_I, S_{IN} and S_{IC} and $\sum S_{VFA}$ if S_A is used in ASM
VFAs (acetate)	S_A	$\sum S_{VFA}$
Particulate inerts[1]	X_I	X_I
SBCOD	X_S	$\sum X_i$ excluding X_I
NH_4^++NH_3 nitrogen	S_{NH}	S_{IN}
Slowly biodegradable organic nitrogen	S_{ND}	none, fit
Particulate biodegradable organic nitrogen	X_{ND}	none, fit[2]
Inorganic carbon	S_{ALK}	S_{IC}

1. Some organics not biodegradable via anaerobic digestion are degradable aerobically. If this is observed empirically (via low levels of inert COD in the effluent), or found experimentally, by biodegradability analysis, some S_I or X_I could be diverted to S_S and X_S, respectively.
2. Can be calculated from N:COD ratios of protein as shown in Appendix D.

Appendix D: Estimating stoichiometric coefficients for fermentation

D.1 STOICHIOMETRIC COEFFICIENTS FROM MONOSACCHARIDE FERMENTATION

The ratios of products from monosaccharide fermentation can be largely simplified by the necessary balancing of elements, and assuming that fermentation proceeds by the three key reactions outlined in Table 3.4 and summarised in Table D.1. Different ratios of acetate/H_2 and propionic acid may result from the second reaction, but for estimation of all four COD products, the different ratios are implicit in the first reaction.

Table D.1: Monosaccharide equations as implemented in the ADM1.

	Products	Reaction
1	Acetate	$C_6H_{12}O_6+2H_2O \rightarrow 2CH_3COOH+2CO_2+4H_2$
2	Acetate, propionate	$3C_6H_{12}O_6 \rightarrow 4CH_3CH_2COOH+2CH_3COOH+2CO_2+2H_2O$
3	Butyrate	$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH+2CO_2+2H_2$

The fraction of monosaccharide which degrades via the first, second and third reactions can be expressed as $\eta_{1,su}$, $\eta_{2,su}$ and $\eta_{3,su}$ respectively, where:

$$\eta_{3,su} = 1 - \eta_{2,su} - \eta_{1,su} \quad \text{(D.1)}$$

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Therefore, the stoichiometric coefficients of each product can be calculated from these fractions, and the relative COD of each product in Table D.1 (see Table D.2). Based on this, the four stoichiometric parameters can be reduced to two parameters, and the COD balance assured. We coded these functions into our implementations for rapid fitting.

Table D.2: Stoichiometric coefficients from monosaccharides uptake, based on Table D.1.

Products	Coefficient
Acetate	$f_{su,ac} = 0.67\ \eta_{1,su} + 0.22\ \eta_{2,su}$
Propionate	$f_{su,pro} = 0.78\ \eta_{2,su}$
Butyrate	$f_{su,but} = 0.83\ (1 - \eta_{2,su} - \eta_{1,su})$
Hydrogen	$f_{su,h2} = 0.33\ \eta_{1,su} + 0.17\ (1 - \eta_{2,su} - \eta_{1,su})$

D.2 STOICHIOMETRIC COEFFICIENTS FROM AMINO ACID FERMENTATION

An initial estimate of the stoichiometric coefficients from amino acid fermentation can be made from the amino acid mix of the primary protein(s), its Stickland donor or acceptor characteristics, and the characteristics of Stickland reactions as described in Section 3.4. The donor/acceptor statuses of the amino acids are shown in Table D.3.

Table D.3: Amino acid Stickland acceptor/donor/uncoupled status (Ramsay 1997).

Amino acid	Form of R group	Donor/acceptor/uncoupled
Glycine	Hydrogen	Acceptor
Alanine	Alkyl	Donor
Valine	Alkyl	Donor
Leucine	Alkyl	Donor/acceptor
Isoleucine	Alkyl	Donor
Serine	Alcohol	Donor
Threonine	Alcohol	Donor/acceptor
Cysteine	Sulphur containing	Donor
Methionine	Sulphur containing	Donor
Proline	Forms ring with amino	Acceptor
Phenylalanine	Aromatic	Donor/acceptor
Tyrosine	Aromatic	Donor/acceptor
Tryptophan	Aromatic	Donor/acceptor
Aspartic acid	Carboxyl	Donor
Glutamic acid	Carboxyl	Donor
Lysine	Nitrogen containing	Donor
Arginine	Nitrogen containing	Donor
Histidine	Nitrogen containing	Uncoupled

Ramsay (1997) compiled the reactions based on this table into a spreadsheet that can be used to predict the products of amino acids (Table D.4). This spreadsheet can be used together with the amino acid content of a protein or protein mix (from analysis or FAO, UN (1970)); the contents for beef flesh and casein in percentage total amino acids are given in Table D4 to predict the stoichiometric yield from a mixture of proteins. While it should not be necessary, the result can be normalised in COD. C_{aa} (the carbon content of the protein) can be analysed by total organic carbon (TOC)/COD analysis, or calculated from the amino acid content.

Table D.4: Products from amino acids based on Stickland reactions (Ramsay 1997).

Amino acid	Molecular formula	HAc	HPr	Hbu	HVa	IN	IC	Other	H_2	ATP	Beef flesh[1]	Casein[1]
Arginine	$C_6H_{14}O_2N_4$	0.5	0.5	0	0.5	4	1	0	–1	1	5.40	2.80
Histidine	$C_6H_9O_2N_3$	1	0	0.5	0	3	1	1	0	2	2.40	2.60
Lysine	$C_6H_{14}O_2N_2$	1	0	1	0	2	0	0	0	1	7.20	6.40
Tyrosine	$C_9H_{11}O_3N$	1	0	0	0	1	1	0.882	1	1	2.70	4.30
Tryptophan	$C_{11}H_{12}O_3N$	0	0	0	0	1	1	1.471	2	1	0.90	0.80
Phenylalanine	$C_9H_{11}O_2N$	0	0	0	0	1	1	1.176	2	1	3.60	4.00
Cysteine	$C_3H_6O_2NS$	1	0	0	0	1	1	0	0.5	1	1.50	0.10
Methionine	$C_5H_{11}O_2NS$	0	1	0	0	1	1	0	1	1	2.00	2.50
Threonine	$C_4H_9O_3N$	1	0	0.5	0	1	0	0	–1	1	4.80	3.90
Serine	$C_3H_7O_3N$	1	0	0	0	1	1	0	1	1	5.70	7.60
Leucine/ Isoleucine	$C_6H_{13}O_2N$	0	0	0	1	1	1	0	2	1	14.40	14.20
Valine	$C_5H_{11}O_2N$	0	0	1	0	1	1	0	2	1	6.50	6.70
Glutamine	$C_5H_9O_4N$	1	0	0.5	0	1	1	0	0	2	13.50	19.20
Aspartate	$C_4H_7O_4N$	1	0	0	0	1	2	0	2	2	8.80	6.40
Glycine	$C_2H_5O_2N$	1	0	0	0	1	0	0	–1	0	8.40	3.00
Alanine	$C_3H_7O_2N$	1	0	0	0	1	1	0	2	1	8.40	4.00
Proline	$C_5H_9O_2N$	0.5	0.5	0	0.5	1	0	0	–1	0	4.00	11.40

Basic units of mole product/mole amino acid. 1. Units of mole % total amino acids.

Table D.5: Calculated products from amino acids.

Source	Acetate $f_{ac,aa}$	Propionate $f_{pro,aa}$	Butyrate $f_{bu,aa}$	Valerate $f_{va,aa}$	IN $f_{IN,aa}$	H_2 $f_{h2,aa}$
Casein	0.33	0.07	0.27	0.26	0.008	0.07
Beef flesh	0.53	0.07	0.19	0.19	0.011	0.02

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Page numbers in *italics* refer to figures and tables.

This Scientific and Technical Report (STR) presents the findings of the IWA Task Group on River Water Quality Modelling (RWQM). The task group was formed to create a scientific and technical base from which to formulate standardized, consistent river water quality models and guidelines for their implementation. This STR presents the first outcome in this effort: River Water Quality Model No. 1 (RWQM1).

As background to the development of River Water Quality Model No. 1, the Task Group completed a critical evaluation of the current state of the practice in water quality modelling. A major limitation in present model formulations is the continued reliance on BOD as the primary state variable, despite the fact that BOD does not include all biodegradable matter. A related difficulty is the poor representation of benthic flux terms. As a result of these shortcomings, it is impossible to close mass balances completely in most existing models. These various limitations in current river water quality models impair their predictive ability in situations of marked changes in a river's pollutant load, streamflow, morphometry, or other basic characteristics.

RWQM1 is intended to serve as a framework for river water quality models that overcome these deficiencies in traditional water quality models and most particularly the failure to close mass balances between the water column and sediment. In addition, the model is intended to be compatible with the existing IWA Activated Sludge Models (STR 9: Activated Sludge Models ASM1, ASM2, ASM2d and ASM3; ISBN: 1900222248) so that it can be straightforwardly linked to them. To these ends, the model incorporates fundamental water quality components and processes to characterise carbon, oxygen, nitrogen, and phosphorus (C, O, N, and P) cycling instead of biochemical oxygen demand as used in traditional models.

The model is presented in terms of processes and components represented via a Petersen stoichiometry matrix, the same approach used for the IWA Activated Sludge Models. The full RWQM1 includes 24 components and 30 processes. The report provides detailed examples on reducing the numbers of components and processes to fit specific water quality problems. Thus, the model provides a framework for both complicated and simplified models. Detailed explanations of the model components, process equations, stoichiometric parameters, and kinetic parameters are provided, as are example parameter values and two case studies.

The STR is intended to launch a participatory process of model development, application, and refinement. RWQM1 provides a framework for this process, but the goal of the Task Group is to involve water quality professionals worldwide in the continued work developing a new water quality modelling approach.

This text will be an invaluable reference for researchers and graduate students specializing in water resources, hydrology, water quality, or environmental modelling in departments of environmental engineering, natural resources, civil engineering, chemical engineering, environmental sciences, and ecology. Water resources engineers, water quality engineers and technical specialists in environmental consultancy, government agencies or regulated industries will also value this critical assessment of the state of practice in water quality modelling.

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