DYNAMIC MODELLING OF ANAEROBIC DIGESTION OF FISCHER-TROPSCH REACTION WATER

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ABSTRACT

Fischer-Tropsch Reaction Water (FTRW) is a high organic strength wastewater produced as a by-product in Sasol's Fischer-Tropsch Reactors. Typically it has an organic load of 18000 mgCOD/L and is highly acidic with a pH of approximately 3.8. It is deficient in nutrients (N and P and other micronutrients).

This dissertation deals with the biological and physico-chemical model development of a dynamic anaerobic digestion model, and explores two different approaches to representing the physico-chemical processes that complement and interact with the bioprocesses. The performances of the resultant two dynamic models (AD-FTRW1 & AD-FTRW2) were compared in order to assess to what extent the more detailed and rigorous ionic speciation modeling in AD-FTRW2 addressed the shortcomings attributed to the simplified physico-chemical modeling in AD-FTRW1.

The ionic speciation model used in AD-FTRW2 uses a classic equilibrium formulation along the same lines as in the UCTADM2 model for anaerobic digestion of municipal wastewater sludges (Brouckaert et al., 2010), while AD-FTRW1 uses a simplification of the approach developed by Musvoto et al. (2000) in order to represent short chain fatty acid (SCFA) dissociation and the weak acid base chemistry of the inorganic carbon system.

A 44 day extract from a 700 day laboratory-scale dataset (Van Zyl et al. 2008) was used as the basis for comparing the models. During this period the membrane bio-reactor was subjected to varying flow and load conditions. To validate the models, the experimentally measured and model predicted process variables of reactor alkalinity, reactor pH, biogas production and effluent SCFA concentration were compared.

It was found that AD-FTRW2 provided superior agreement with pH data, but predictions of alkalinity, gas production rate and effluent short-chain fatty acids were not significantly improved in AD-FTRW2 relative to AD-FTRW1. This outcome was hypothesized since pH is strongly dependent on physico-chemical processes such as ionic interactions in solution and gas exchange which were the components to the models (AD-FTRW1 versus AD-FTRW2) which differed most significantly. Alkalinity, which is also highly influenced by physico-chemical model representations showed substantial improvement however statistical analysis could not show this improvement to be significant. The other two variables that were compared, biogas production and effluent SCFA concentration, displayed very similar agreement with experimental data. These variables depend more on mass balance effects and biological kinetics and were therefore not significantly altered by the more rigorous handling of aqueous chemistry in AD-FTRW2. It was concluded that AD-FTRW2 constitutes an improvement in model predictive power over AD-FTRW1 at a small cost in computing time.

DECLARATIONS

Supervisor's Declaration:

As the candidate's supervisor, I hereby declare that this dissertation is fit for submission.

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Student's Declaration:

I, Crispian McLintock Lees, declare that:

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Abbreviations

AD	Anaerobic Digestion
ADFTRW	Anaerobic Digestion of Fischer-Tropsch Reaction Water
AD-FTRW1	Anaerobic Digestion of Fischer-Tropsch Reaction Water Model 1
AD-FTRW2	Anaerobic Digestion of Fischer-Tropsch Reaction Water Model 2
AnMBR	Anaerobic Membrane Bioreactor
API	American Petroleum Industries waste water
COD	Chemical Oxygen Demand
CTL	Coal to liquids
FOG	Functional Organism Group
FSA	Free and Saline Ammonia
FT	Fischer-Tropsch
FTRW	Fischer-Tropsch Reaction Water
GTL	Gas to liquid
HRT	Hydraulic Retention Time
IWA	International Water Association
ME	Mean Error
MLSS	Mixed Liquor Suspended Solids
MSRE	Mean Square Relative Error
OLR	Organic Loading Rate
PBIAS	Percent Bias
RMSD	Root Mean Squared Deviation
SCFA	Short Chain Fatty Acid
UCTADM2	University of Cape Town Anaerobic Digestion Model 2
WABC	Weak Acid/Base Chemistry
WWTP	Waste Water Treatment Plant

Symbols

$[H_2]$	Dissolved hydrogen concentration
[SCFA]	SCFA concentration
μ_j	Specific growth rate
μ_{max}	Maximum specific growth rate
Ac	Acetic acid
acBu	Butyric acid acetogenesis
acEt	Ethanol acetogenesis
acHx	hexanoic acid acetogenesis
acPr	Propionic acid acetogenesis
acVa	Valeric acid acetogenesis
ad	hydrolysis and acidogenesis
am	Acetoclastic Methanogenesis
b_j	Rate of endogenous decay
Bu	Butyric acid
Ca	Calcium
CH_4	Methane
CO_2	Carbon dioxide
γ_b	Electron accepting capacity of the biomass
γ_s	Electron donating capacity of the substrate
E	Fraction of the Biodegradable COD that is converted to Biomass
EtOH	Ethanol
f	Unbiodegradable fraction of endogenous biomass
F	Fraction of Organic Acid in dissociated form
fd	Formate digestion
Fm	Formic acid
hm	Hydrogenotrophic Methanogenesis
Hx	Hexanoic acid
I_n	Inhibition function
k_{Ij}	Inhibition constant
K_{sj}	Half saturation constant
K_i	Inhibition constant
MeOH	Methanol
mm	Methanol Methanogenesis
NaOH	Sodium hydroxide
pH_{LLZj}	Lower-limit pH of 50% inhibition for active mass Z_j
pH_r	Reactor pH
pH_{ULZj}	Upper-limit pH of 50% inhibition for active mass Z_j
Pr	Propionic acid
r_j	Reaction rate
R_s	Sludge age
S_{be}	Effluent COD
S_{bi}	Influent COD
S_{bp}	Biodegradable particulate matter
S_j	Substrate Concentration

S_i	Inhibitory substrate concentration
S_m	Biogas
T_{LL}	Lower-limit temperature of 50% inhibition
T_r	Reactor temperature
T_{UL}	Upper-limit temperature of 50% inhibition
Va	Valeric acid
Y_j	Biomass Yield
Z_{aj}	Active mass concentration
Z_e	Endogenous residue
Z_{VSS}	Biomass
Z_{xx}	Biomass (function depicted in the subscript)

GLOSSARY

acetogenesis	The biologically mediated, anaerobic breakdown of a variety of carbon sources to form acetate
acetoclastic methanogenesis	The biologically mediated anaerobic process whereby acetate is broken down to form methane and promote biomass growth
hydrogenotrophic methanogenesis	The biologically mediated anaerobic process whereby hydrogen and carbon dioxide are utilized to form methane and promote biomass growth
long chain fatty acids	Carboxylic acids with aliphatic tails of between 13 and 21 carbon atoms.
Mesophilic	Refers to a moderate operational temperature range of between 20°C and 40°C. A temperature of 37°C is typical.
short chain fatty acids	Carboxylic acids with a carbon number less than or equal to 6: hexanoic acid, valeric acid, butanoic acid, propionic acid, acetic acid, formic acid
MinteqA2	An aquatic chemistry software package with a comprehensive database of equilibrium constants for commonly occurring aquatic ionic species.

1 INTRODUCTION

1.1 Purpose of the study

This study adopts a modelling approach and aims to develop a dynamic anaerobic digestion reactor model suited to the anaerobic treatment of Sasol's Fischer-Tropsch Reaction Water.

The interaction between the biological processes and the physico-chemical processes in anaerobic digestion has been shown to be very significant. In order to model anaerobic digestion adequately, this interaction needs to be sufficiently represented through accurate ionic speciation modelling and biological reaction kinetic inhibitions. A comprehensive biological model for the anaerobic digestion of Fischer-Tropsch reaction water (AD-FTRW1) has been developed but a shortcoming has been identified in the integrated physico-chemical model. The model was developed under the assumption that the pH in an Anaerobic Digestion of Fischer-Tropsch Reaction Water (ADFTRW) reactor will remain in the range of 6.5 – 7.5. This is the major limitation of AD-FTRW1.

In response to this shortcoming, this work aims to improve the previously developed dynamic model (AD-FTRW1) by integrating a more comprehensive ionic speciation sub-model. The ionic speciation sub-model considers all the relevant acid/base subsystems, and extends the pH range (3.5 to 9) for which the model can produce meaningful results.

The resultant model, referred to henceforth as AD-FTRW2, (given a fully characterized feed, dosage and wastage schedule) should be able to accurately predict significant process variables and effluent characteristics such as pH, alkalinity, biogas production, biogas composition and effluent COD. In application, the purpose of the model will be to assist in experimental design, process design and advanced model-based process control.

Specific to this study, the research question raised is;

Can the pH prediction in AD-FTRW1 be improved through the incorporation of a more comprehensive ionic speciation model?

The corresponding hypothesis is;

The pH prediction in AD-FTRW1 will be improved through the incorporation of a more comprehensive ionic speciation model.

To answer the research question and test the abovementioned hypothesis, a 44 day extract from a 700 day laboratory-scale dataset (Van Zyl et al. 2008) was simulated with both AD-FTRW1 and AD-FTRW2. During this period the membrane bio-reactor was subjected to varying flow and load conditions. The relative agreement of the simulated outputs as compared to the experimental outputs was then assessed statistically to determine whether the revised model (AD-FTRW2) gave significantly better predictions than its predecessor (AD-FTRW1).

1.2 Context of the study

This research is of particular interest to Sasol Ltd, a South African company involved in the petro-chemical industry whose operations produce large volumes of Fischer-Tropsch Reaction Water.

Sasol is responsible for supplying a large percentage of South Africa's fuel demand. Their Synthetic Fuels plants based in Secunda and Sasolburg produce large volumes of industrial wastewater on a daily basis; 128 Ml/day at Secunda (Phillips and du Toit 2002). Secunda's wastewater is heavily contaminated with a chemical oxygen demand of approximately 677 ton/day. This corresponds to approximately a 7 million person equivalent organic load and it necessitates treatment of the wastewater prior to it being recycled into the process as process cooling water (Phillips and du Toit 2002). Sasol's aim of zero liquid effluent discharge connects waste water treatment efficiency to production rate via process cooling efficiency as this is directly impacted by the purity of the process cooling water which is sourced partially from Sasol's treated waste water stream. This places Sasol's wastewater treatment facilities in a demanding position where not only are their works driven by legislation in the form of effluent discharge limits but they are also motivated to run efficiently by their strong interaction with production and therefore profits.

Two major processes which contribute to Sasol's wastewater load are the Fischer-Tropsch reactors (where water is chemically produced as a byproduct) and SYNGAS Clean-up (where water is used as a stripping/quenching medium to cool the SYNGAS and cleanse it of unwanted volatile hydrocarbons and other impurities). These large waste water streams are referred to as Fischer-Tropsch Reaction Water (FTRW) and Stripped Gas Liquor (SGL) respectively.

Currently Sasol's industrial waste water (at their Secunda site) is treated aerobically in an activated sludge plant which is the 2nd largest in the world. The option of Mesophilic Anaerobic digestion of a portion of the waste water stream is being investigated due to some significant operational and cost benefits and due to the amenability of Fischer Tropsch Reaction Water to this process.

The major potential advantages of Anaerobic Digestion of Fischer-Tropsch Reaction Water (ADFTRW) include reduced energy input (due to zero requirement for aeration), energy recovery through biogas production, reduced sludge production and a smaller land requirement. This all translates into a reduced environmental footprint.

The major operational drawback to anaerobic digestion is control. Anaerobic systems do not respond well to process fluctuations and are only effective within small margins of operating conditions such as pH, temperature and dissolved hydrogen concentration. If not properly managed, anaerobic digesters are prone to failure resulting in difficult effluent management scenarios.

With this in mind, this study aims to develop and integrate two existing Anaerobic Digestion (Sasol Technology's Biological model) and Ionic Speciation models (UKZN's Ionic speciation model) to assist in the

development and design of ADFTRW facilities and to enhance disturbance rejection[1] through state of the art process control. The model will be validated against existing lab-scale data supplied by Sasol.

The research forms part of work undertaken by the Pollution Research Group and Sasol Ltd, as part of Sasol's University Collaborative Programme.

1.3 Research Outcomes

An integrated Ionic Speciation and Biological Dynamic Model of Mesophilic Anaerobic Digestion of Fischer-Tropsch Reaction Water. The model shall be referred to henceforth as AD-FTRW2.

- The model must display a reasonable degree of accuracy in its predictive capacity as proven through a model validation procedure.
- The model should be able to predict significant process variables and effluent characteristics such as pH, alkalinity, biogas production, biogas composition and effluent COD.

1.4 Significance of the study

The benefits of generating this process model (AD-FTRW2) will be the

- Reduction of experimental effort through combined experimentation and simulation in the context of optimal experimental design.
- Ability to model Sasol effluent treatment processes for existing installations and proposed new installations for improved design, control, operation and troubleshooting.
- Optimisation of Sasol's water treatment network through the concept of ADFTRW
- Alignment of ADFTRW with new technology sales requirements which require a process model with the sale of a process design.

The specific outcome of integrating a more comprehensive ionic speciation model into an anaerobic digestion model, hopes to overcome (to an extent) a short-coming in preceding AD models which did not exhibit sufficient accuracy in their physico-chemical models and in turn represented the interaction between the physico-chemical and biological processes poorly. The study will adopt the UCT strategy of waste water stream representation by virtue of the fact that it is a development of AD-FTRW1 which adopted this approach and it therefore offers further testing of this method of waste water stream representation.

[1] Disturbance Rejection: The ability of a process to maintain a prescribed level of operation (e.g effluent COD concentration) when subjected to large fluctuations in input characteristics and variables.

1.5 Limitations of the study

The scope of the modelling is specific to high temperature Fischer-Tropsch reaction water. High temperature Fischer-Tropsch reaction water is produced when the Fischer-Tropsch (FT) reaction takes place at high temperature over an iron catalyst, and is higher in Short Chain Fatty Acids (SCFA's) than alcohols, while low temperature Fischer-Tropsch reaction water, which is characteristic of more recent installations where the FT reaction takes place over a cobalt catalyst at a lower temperature, has a higher alcohol content relative to short chain fatty acids. The reason for this specific focus is that the initial commercialization of anaerobic digestion of FTRW is intended for the Secunda plant and therefore needs to be compatible with its existing infrastructure. At the Secunda plant high temperature Fischer-Tropsch reactors are employed in the polymerization of SYNGAS. With this being said, it is hoped that the model can be easily modified to represent the digestion of low temperature Fischer-Tropsch reaction water. The model is further restricted to mesophilic anaerobic digestion.

2 LITERATURE REVIEW

2.1 Introduction

The literature review has been constructed to cover four major topics that form the basis to this study.

The review begins by taking a broad look at the typical functioning of a Wastewater Treatment Works via a plant-wide modelling framework known as Benchmark Simulation Model 2. The various unit operations involved in the process are explored briefly to establish their individual functions and to discover which models are used conventionally for their representation. This section lends context to anaerobic digestion as a treatment process and helps to establish the shift toward a more plant-wide modelling approach.

Thereafter, the company Sasol will be reviewed with a focus on their synfuels process and the applicability of this research to their industrial waste water streams. Out of this section, the significance of the study is elucidated in terms of the optimization of Sasol's water treatment network through the concept of ADFTRW.

This will be followed by a process overview of anaerobic digestion (AD). The overview will include the mechanisms involved in the anaerobic biological reactions, together with an explanation of significant process variables and inhibitory factors.

Lastly, the literature review will look closely at the current trends in anaerobic digestion modelling and the previous modelling work upon which this research is based. A detailed look at anaerobic digestion reaction stoichiometry and kinetics will be carried out via a comprehensive analysis of AD-FTRW1. Out of this section, our research question is distilled and this relates to the possibility for improvement within existing AD models in the area of ionic speciation.

2.2 Wastewater Treatment Works

2.2.1 *Plant-wide Modelling*

A model can be defined as anything which is capable of generating behaviour resembling the behaviour of a system within its experimental frame (Kops et al., 1999). The fundamental importance of modelling of chemical processes is that it enables increased understanding of the underlying mechanisms involved in the process and it enhances process design, control and optimization through its predictive capabilities.

Modelling, control and optimization of wastewater treatment unit operations has historically been undertaken in an isolated/independent manner, where the influence of various control strategies on the efficacy of downstream processes has been neglected in determining which control route to take on a local (single unit operation) level. This approach often leads to sub-optimization and consequently reduced effluent quality or increased operating costs (Rosen et al., 2005). In recent times a drive towards a plant-wide modelling approach has been recognised

by researchers as a more beneficial outlook in optimizing the performance of a wastewater treatment facility. This more holistic approach consists of local models for each unit operation, which are then overseen by supervisory control systems which take into account the interactions between all of the sub-processes.

Initiated by Working Groups of COST Action 682 and 624 and then continued by the International Water Association's (IWA) Task Group on Benchmarking of Control Strategies for wastewater treatment plants (WWTP's), plant-wide simulation benchmarks began with the development of Benchmark Simulation Model 1 (BSM1). This benchmark focused on evaluating control strategies for activated sludge. The plant layout in BSM1 consists of a five-compartment activated sludge reactor consisting of two anoxic tanks followed by three aerobic tanks. The activated sludge unit is then followed by a secondary clarifier. In this way the model simulates nitrification and denitrification in a configuration commonly encountered in WWTPs.

It was apparent that, while BSM1 was a step in the right direction in terms of plant-wide modelling, it still did not represent a true plant-wide benchmark model. Subsequently Benchmark Simulation Model 2 (BSM2) was developed. As with BSM1, it includes a model, control system, a benchmarking procedure and evaluation criteria. The model's plant layout is far more comprehensive and describes a wastewater treatment plant consisting of a primary clarifier, a five-tank activated sludge system with a non-reactive secondary clarifier (as in BSM1), a sludge thickener, an anaerobic digester and a dewatering unit (Jeppsson et al., 2007). The slow dynamics of anaerobic digestion (which is represented in the sludge train) made it necessary to increase the length of the evaluation period in BSM2. This necessitated the incorporation of seasonal effects on the WWTP with respect to temperature variations and changing influent flow-rate patterns (Jeppsson et al., 2007). Plant unit operations and the type of model descriptions thereof are presented in the table below along with a brief outline of the function of each unit.

Table 1: BSM2 Unit Operations and Description

No:	*Unit Operation*	*Model Representation*	*Function*
1	*Primary Clarifier*	Otterpohl and Freund (1992)	solid-liquid separation
			50% solids removal
			no biological activity
2	*5-Reactor Activated Sludge System*	ASM1	COD Removal
			Biological Nitrogen Removal
			Nitrification
			Denitrification
3	*Secondary Clarifier*	Takacs (1991)	solid-liquid separation
			no biological activity
4	*Gravity Thickening*	Ideal, Continuous Model	solid-liquid separation
			98% solids removal efficiency
			no biological activity
5	*Anaerobic Digestion*	ADM1	Sludge Stabilization
			COD Removal
			Hydrolysis
			Acidogenesis
			Acetogenesis
			Methanogenesis
6	*Dewatering*	Ideal, Continuous Model	solid-liquid separation
			98% solids removal efficiency

(Jeppsson et al., 2007)

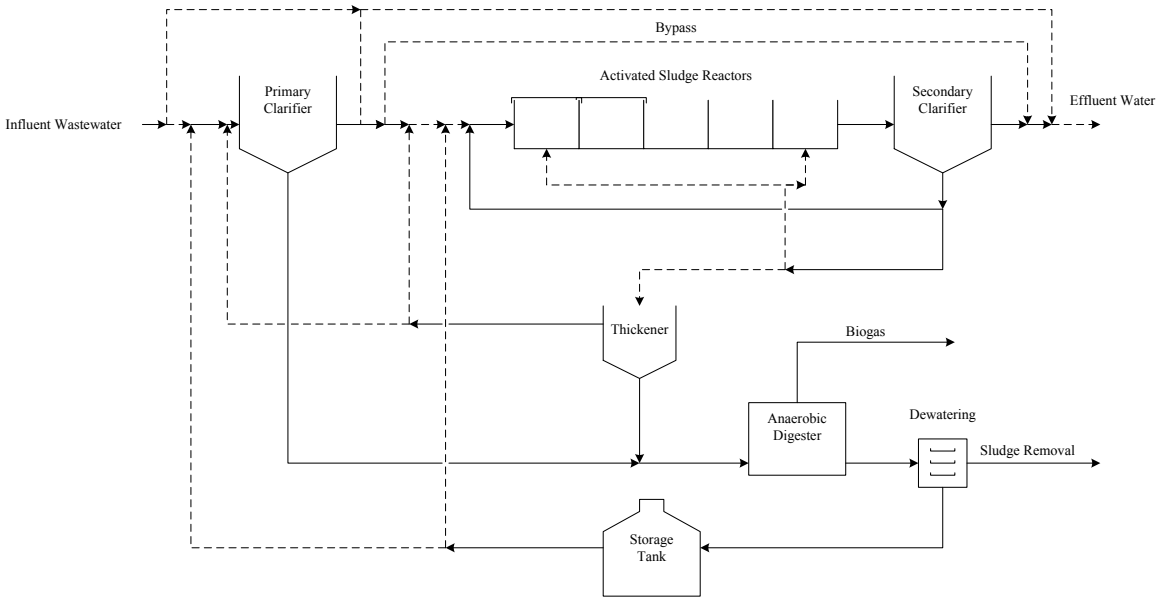

Figure 1: BSM2 Plant Layout

2.3 Sasol

2.3.1 *Core Business*

In 1955 Sasol, the "**S**uid **A**frikaanse **S**teenkool en **Ol**ie Maatskapy," produced its first automotive fuel from Sasol 1; the company's first CTL plant based in Sasolburg (Hall-Green 2000). The company's proprietary technology is involved in the upgrading of raw coal (mined in the surrounding areas) and natural gas into liquid petroleum products. This is achieved in 4 major process steps:

1) Coal gasification / Auto-thermal reforming

2) Fischer-Tropsch Reaction

3) Product Separation

4) Product Upgrading

In an ongoing drive towards process optimization and by-product utilization, Sasol has become involved in various other chemical industries such as polymers (e.g. ethylene, waxes), fertilizers and explosives. But the major portion of their business remains in the Synfuels industry.

At the heart of the Synfuels and Polymer's processes are Sasol's Fischer-Tropsch Reactors. The reactors are fundamentally based on the work of two chemists, Franz Fischer and Hans Tropsch, who discovered a chemical reaction to convert coal and gas into liquid fuels during the 1920's (Gross 2006). The Fischer-Tropsch reaction produces hydrocarbons and water from a carbon monoxide and hydrogen feed gas as is depicted below:

$$nCO + 2nH_2 \xrightarrow{catalyst} C_nH_{2n} + nH_2O$$

Equation 1: Fischer-Tropsch Reaction

The hydrocarbons (including methane) are separated and upgraded through processes such as alkylation, polymerization and reforming to value added marketable products.

The chemically produced water is called Fischer-Tropsch Reaction Water and forms a major contributor to Sasol's wastewater treatment load as it is contaminated with soluble organic reaction products; mostly oxygenated organics such as alcohols and short chain fatty acids.

Another significant contributor to the wastewater treatment load is stripped gas liquor (SGL). SGL comes from SYNGAS cleanup/cooling, where steam is used as a stripping/quenching medium to strip the SYNGAS of unwanted impurities and cool it down before the SYNGAS is routed to the waste heat boilers and then the Fischer-Tropsch Reactors.

2.3.2 *Wastewater Treatment System Configuration at Secunda*

At Sasol's Secunda site, the three major wastewater streams (Oily sewer water, SGL and FTRW) were designed to be combined and treated in a fully aerobic, activated sludge plant. This configuration has significant operational and cost disadvantages such as:

- High oxygen requirements for aeration and electricity generation
- High energy requirements for aeration
- Large production of biomass and sludge with poor settling qualities
- High solid/liquid separation cost
- Poor effluent quality.

As part of a notion to optimize the wastewater treatment process, it has been recognized that FTRW (which constitutes 77% of the organic load but 23% of the volumetric load) is amenable to anaerobic digestion. If FTRW could be successfully treated anaerobically, this would lead to major operational cost reduction from decreased energy requirements for aeration and decreased sludge production.

Table 2: Sasol's Waste Water Streams at Secunda

Wastewater Stream	***Volumetric Load***		***Organic Load (COD)***	
	Ml/d	***%***	***tonO_2/d***	***%***
FTRW	29	23	522	77
SGL	62	48	99.2	15
API/Oily Sewer Water	37	29	55.5	8
Total	128	100	676.7	100

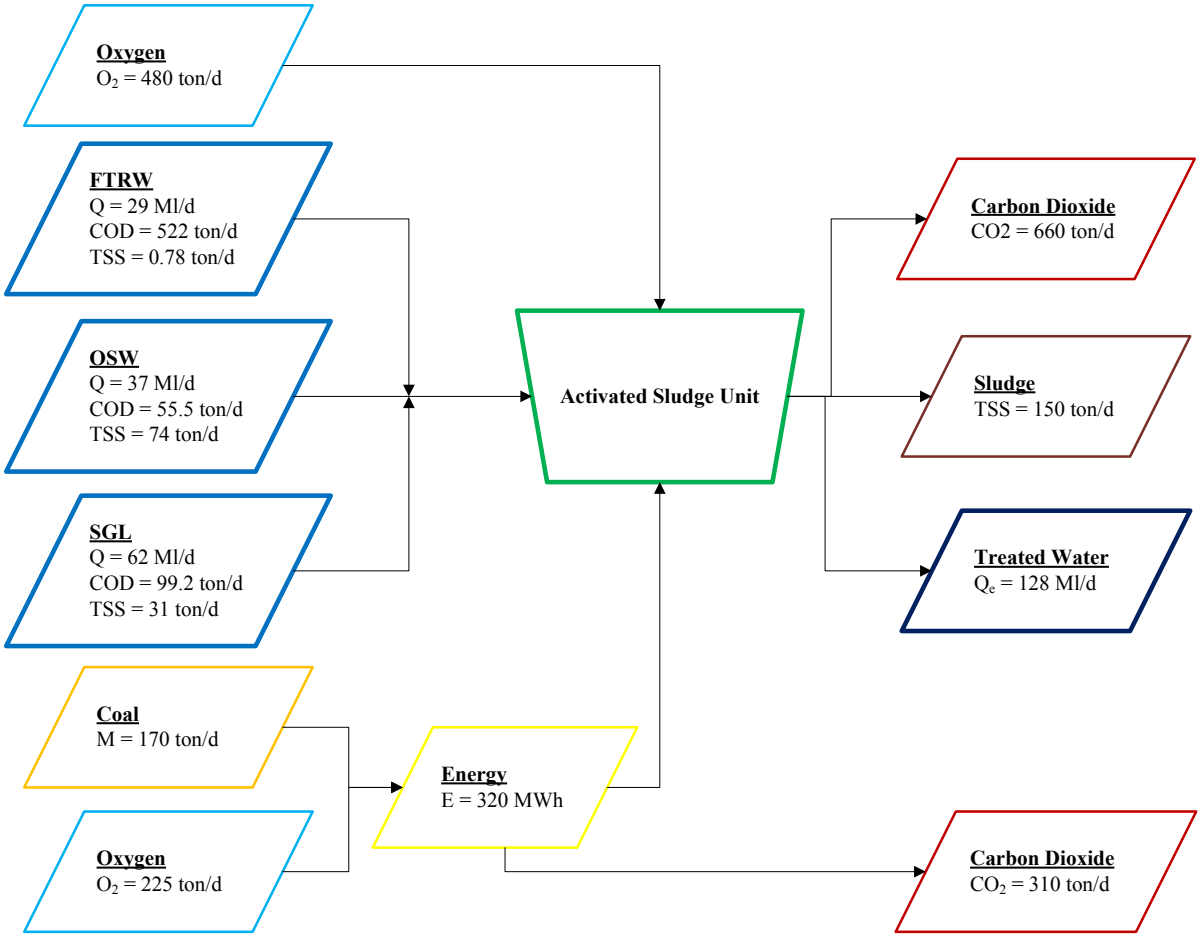

Figure 2: Organic Loading and Energy Requirement for Sasol's Secunda WWTP.

(van Zyl 2008)

2.3.3 *Fischer-Tropsch Reaction Water*

FTRW is a chemically produced by-product of the Fischer-Tropsch reaction (Equation 1). It consists of water contaminated predominantly with oxygenated organics such as short chain fatty acids (SCFA's) and alcohols. Due to its chemically produced origin, it is also very low in dissolved salts and particulates. Research has shown that FTRW is amenable to Anaerobic Digestion due to its high content of readily biodegradable SCFA's (van Zyl 2008) so long as it is complemented with sufficient nitrogen, alkalinity and nutrient dosing.

Two types of FTRW exist with reference to Sasol's plants, high temperature Fischer-Tropsch reaction water and low temperature Fischer-Tropsch reaction water which emanate from processes of the same name respectively. High temperature Fischer-Tropsch reaction water is higher in SCFA's than alcohols, while low temperature Fischer-Tropsch reaction water which is characteristic of more recent installations has a higher alcohol content relative to SCFA's. This study is specific to high temperature Fischer-Tropsch reaction water sourced from the

Secunda synfuels plants (Sasol 2 and Sasol 3). Below is a table of the significant properties of high temperature Fischer-Tropsch reaction water.

Table 3: Properties of High Temperature Fischer Tropsch Reaction Water.

Property	***High Temperature FTRW***
Constituent Components	Water, C2-C6 Organic Acids, C1-C2 Alcohols
Chemical Oxygen Demand (mg/l)	18000
Total Dissolved Solids (mg/l)	35
pH	3.77

(van Zyl 2008)

2.3.4 *Stripped Gas Liquor*

SGL comes from SYNGAS cleanup/cooling, where steam is used as a stripping/quenching medium to strip the SYNGAS of unwanted impurities and cool it down before the gas is fed to waste heat boilers and then the Fischer-Tropsch Reactors. During gasification a significant quantity of ammonia is produced and, due to its high aqueous solubility, practically all of the ammonia can be found dissolved in the SGL. Other constituents of SGL include hydrocyanic acid, tar, oils, phenols and other refractory components.

2.4 Anaerobic Digestion

This section on anaerobic digestion starts with a process overview and is then followed by a process description from a mechanistic perspective.

2.4.1 *Overview*

The main goals of wastewater treatment operations are to:

1) Achieve an average reduction in nutrient levels (COD, macro and micronutrients) and
2) Achieve adequate disturbance rejection (i.e. achieve good effluent qualities in spite of many disturbances).

Anaerobic digestion is the most common method of sludge stabilization in municipal waste water treatment and is also effective in reducing sludge volumes with the production of energy-rich biogas (Sotemann et al., 2006). The major advantages of AD over other biological unit operations according to Batstone et al. (2002) include:

1) High organic loading rates

2) Low sludge production
3) Net positive energy production from biogas
4) Greenhouse gas reduction through the replacement of fossil fuels by biogas.

2.4.2 *Process Description*

In the absence of terminal electron acceptors such as O_2, NO_3^{2-} or SO_4^{2-}, anaerobic conditions prevail. Under these conditions, micro-organisms use biodegradable organics as electron donors (a carbon source) and, as a result of the process, CO_2 and methane are produced along with energy used for biomass growth. Methane contains a significant portion of the energy and electrons made available by the original organics, while the micro-organisms receive very little of the available energy. This translates into slow growth rates for the biomass, greatly reducing sludge disposal costs as compared to aerobic treatment. Another advantage of the process is its yield of methane which can be used as a renewable energy source. Figure 3 below describes the process of anaerobic digestion in more detail and explores the micro-organisms involved at each trophic level.

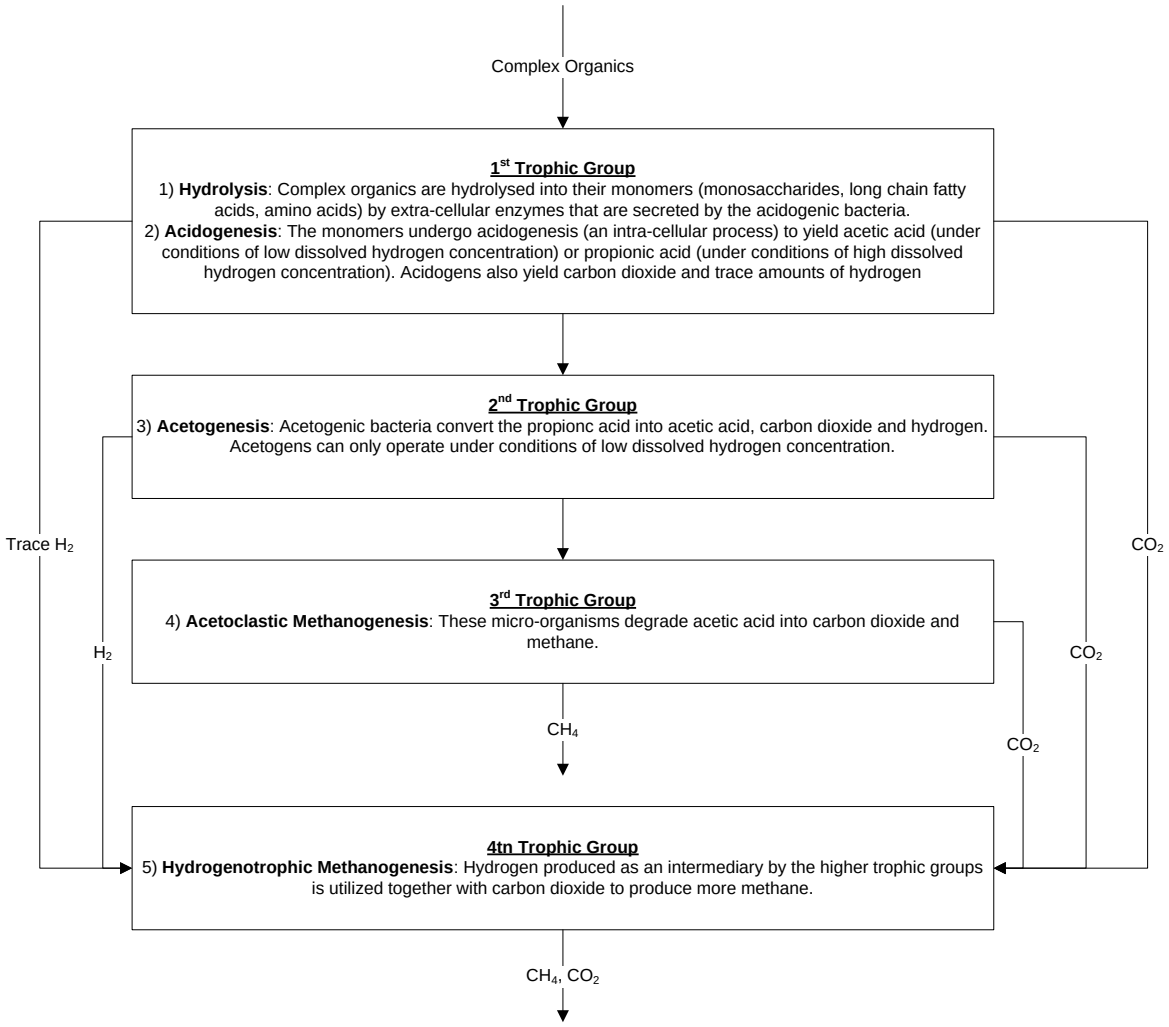

Figure 3: Anaerobic Digestion Process Overview

2.5 Anaerobic Digestion Modelling

This section reviews the theory relevant to the modelling of anaerobic digestion. Following an overview on the importance of modelling anaerobic digestion, it continues with a literature review on two established AD models; ADM1 and UCTADM1. Specific focus is then ascribed to the mathematical modelling techniques used to describe reaction stoichiometry, biological uptake and inhibition kinetics before the previous work on which this work is based is reviewed in detail (AD-FTRW1 and UKZN's ionic speciation model).

2.5.1 *Overview*

Anaerobic digestion is a widespread wastewater treatment application. But despite this fact, the design, operation and control of anaerobic digesters is still based predominantly on empirical guidelines and experience. Mathematical models form the basis of advanced control. Accurate predictive mathematical modelling and simulation of anaerobic digestion is an invaluable tool in process evaluation and in process operation in order to achieve an appropriate level of disturbance rejection (which historically has been anaerobic digestion's major shortcoming) (Sotemann et al., 2006). The modelling of wastewater treatment systems includes many chemical and physical processes, and anaerobic digestion modelling is no exception. Hydraulics (characterized in mixed systems by Hydraulic Retention Times or HRT's), hydrodynamics, nutrient reactions coupled with biomass growth, mass transfer and ionic speciation are all processes whose inclusion in a dynamic model is dependent on the specific system being modelled, the model complexity required and the predictive horizon specified (Olsson and Newell 1999). In terms of anaerobic digestion modelling, all of the above-mentioned processes are included except for the hydrodynamics of the system. The motivation for this simplification is that most anaerobic digesters are mechanically mixed and due to their large hydraulic retention times, they can be reasonably approximated by a perfectly mixed tank.

The IWA Anaerobic Digestion Modelling Task Group was formed in 1977 at the 8th World Congress on anaerobic digestion with the primary objective of formulating a generalized anaerobic digestion model. As a product of this initiative the IWA "Anaerobic Digestion Model No. 1" (ADM1) was presented in 2002 by Batstone et al. and was widely regarded as a breakthrough in the field of anaerobic digestion modelling (Rosen et al., 2005).

a. ***Summary of ADM1***

ADM1 has largely catalysed the progression of the AD modelling field. The general structure of the biological model is outlined in Figure 4 below.

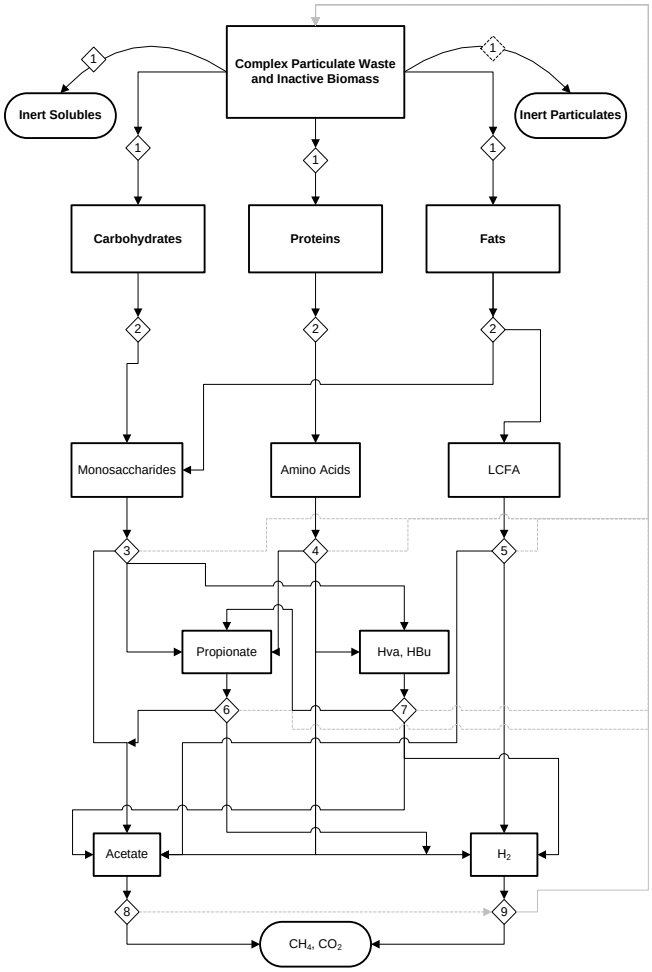

Figure 4: Biological model structure of ADM1

(Batstone et al., 2002)

With reference to Figure 4, the biological model structure of ADM1 is discussed below:

Complex particulate waste and inactive biomass is first characterized according to its biodegradability into inert solubles (indigestible), inert particulates (indigestible), and then into its biodegradable fraction. The biodegradable fraction is further characterized into its protein, carbohydrate and lipid content.

1) Characterization is understood to occur during an array of processes collectively referred to as disintegration. Disintegration could include processes such as lysis, non-enzymatic decay, phase separation and physical breakdown such as shearing (Batstone et al., 2002).
2) Following disintegration, proteins, carbohydrates and lipids are further broken down into their soluble monomers (amino acids, monosaccharide's and long-chain fatty acids respectively) via hydrolysis.

Note: Step 1) and 2) are extracellular steps and are only partly biologically mediated. Hydrolysis is biologically mediated by enzymatic secretions from the micro-organisms, while the remaining processes which make up disintegration are not biologically co-ordinated.

3) The acidogenesis of monosaccharides into mixed organic acids, hydrogen and carbon dioxide is an intracellular process carried out by a specific acidogenic trophic group of micro-organisms according to the model representation.
4) The process of acidogenesis of amino acids is similar to process 3 above but is carried out by a separate acidogenic trophic group according to the model description.
5) Process 5 represents acetogenesis from long-chain fatty acids.
6) Process 6 represents acetogenesis from propionate.
7) Process 7 represents acetogenesis from short chain fatty acids
8) Process 8 represents acetoclastic methanogenesis
9) Process 9 represents hydrogenotrophic methanogenesis

Note: Steps 3) to 9) are intracellular steps which lead to biomass growth. Each trophic group is also subject to biomass decay. Inactive biomass is recycled to the first stage of the model (characterization), where it becomes digestible substrate.

Also included in the model are significant physico-chemical reactions which interact with the biological processes as they contribute to the environment within which the microorganisms exist. The physico-chemical steps which are included are ion association/dissociation and gas-liquid mass transfer. ADM1 does not however account for non-idealities in the liquid phase and the lack of ion activity correction (at low conductivity), ion pairing (at high conductivity), precipitation and phosphorous modelling are identified as significant limitations of the model (Batstone et al., 2012). These limitations have significant impact on the applicability of the pH prediction method in ADM1which only validates it for dilute systems and precludes it from modelling digester failure. It has been identified by Batstone et al. (2012) that for anaerobic digester liquors it is necessary to employ full iterative ion activity correction in order to achieve a pH prediction error of less than 5%. Since ADM1 does not include ion activity correction, this implies that the current accuracy of the pH prediction system in ADM1 is greater than 5% error.

The ADM1 model does not, however, include liquid-solid (precipitation) reactions. The reason for the exclusion of precipitation reactions from this model was due to their complexity and the fact that existing models in that area were relatively recent and untested at the time of the model development. It must be noted, however, that liquid-solid reactions become significant in systems with high levels of cations and especially so with those that readily form carbonate precipitates such as Mg^{2+} and Ca^{2+} (Batstone et al., 2002).

Biological inhibitions represented in the model include pH inhibition which affects all trophic groups, hydrogen inhibition which affects the acetogenic trophic groups and free ammonia inhibition which affects the acetoclastic methanogenic trophic group.

The major challenge posed by ADM1, however, lay in its method of sludge characterization as it made the model difficult to apply in industrial applications. Sludge was characterized by determining and defining its carbohydrate, lipid and protein content; all of which are measurements that are not routinely available on sewage sludges (Sotemann et al., 2006). In response to this, the Water Research Group of the University of

Cape Town proposed a different model for anaerobic digestion, UCTADM1, which characterized sludge in terms of its COD and its C, H, O and N composition.

b. ***Summary of UCTADM1***

The model describes the influent sludge in terms of a sludge specific generic formula proposed by McCarty (1972) of the form $C_XH_YO_ZN_AP_B$. The model then describes the digestion of the sludge by first hydrolysis to glucose and secondly acidogenesis to short chain fatty acids. While the model makes a significant simplification with use of the so-called "glucose pipeline", little loss of accuracy is incurred since the products of hydrolysis followed by acidogenesis remain the same as for lipids, proteins and carbohydrates as short chain fatty acids (Sotemann et al., 2006). Further to this fact that the stoichiometric representation of the final products should be correct, so long as the rate limiting step is modelled with a reasonable kinetic representation the kinetics of the other sub-processes become of less importance making the "glucose pipeline" assumption less influential on the overall performance of the model.

c. ***Importance of physico-chemical processes and their implementation***

During the early stages of anaerobic digestion modelling, focus was confined to the biological processes that carried out the digestion process. The interaction of the biological processes with the physico-chemical states of the digestion system was identified at an early stage as a very important consideration due to the significant and inhibitory effects of pH on biological processes.

The major importance of modelling the physico-chemical system according to Batstone et al. (2002) is that it permits the;

- Expression of biological inhibition factors such as pH, free acids and bases, and dissolved gas concentrations.
- Prediction of major performance variables such as gas flow and carbon alkalinity.
- Calculation of the control set point for pH which has major implications on operating costs as dosage for pH control is the major operating cost in an AD system.

Musvoto et al. (1997) developed a kinetic based model for mixed acid/base systems which has found extensive application in anaerobic digestion models.

2.5.2 *Mathematical Techniques*

a. ***Stoichiometry***

Micro-organism metabolism is made up of catabolic and anabolic reactions. Catabolism refers to the process whereby complex molecules are broken down into simpler ones with the release of energy, while anabolism refers to the process whereby complex molecules are synthesized from simpler ones with the storage of energy (Henze 2008). The mathematical link between the catabolic and anabolic reactions is the fraction of

biodegradable COD that is converted to biomass and is denoted by the parameter "Y" known as the true organism yield.

b. ***Process Kinetics***

i. **Substrate Uptake**

Kinetics of biological reactions in waste water treatment processes are regularly described using Monod kinetics (Sotemann et al., 2006). Otherwise referred to as Michaelis-Menten kinetics, Monod kinetics describe the uptake of soluble substrate by the micro-organisms.

$$r_j = \mu_j Z_{Aj} = \frac{\mu_{\max\ j} S_j}{(K_{sj} + S_j)} Z_{Aj}$$

Equation 2: Monod Kinetics

Once the substrate uptake rate is adequately modelled, the biomass growth rate can be easily related via the biomass yield parameter (Y). This is often referred to as Monod Yield Kinetics. The generalized form of this kinetic expression is displayed below:

$$r_j = \mu_j . Y . Z_{Aj} = \frac{\mu_{\max\ j} S_j}{(K_{sj} + S_j)} . Y . Z_{Aj}$$

Equation 3: Monod Yield Kinetics

Another form of substrate uptake kinetics is the Haldane kinetic expression. Haldane kinetics are suitable where high soluble substrate concentrations impose an inhibitory affect on the reaction of which they form a reactant.

$$r_j = \mu_j Z_{Aj} = \frac{S_j}{(K_{sj} + S_j + \frac{S_j^2}{K_I})} . Z_{Aj}$$

Equation 4: Haldane Kinetics

ii. **Inhibition**

The general method for applying inhibitory effects to kinetics is by attaching inhibition functions as a product to the growth/uptake kinetics. This can be shown via the generalised Monod kinetics proposed during the development of ADM1 (Batstone et al., 2002).

$$r_j = \mu_j Z_{Aj} . I_1 . (\ldots) I_n = \frac{\mu_{\max\ j} S_j}{(K_{sj} + S_j)} Z_{Aj} . I_1 . (\ldots) I_n$$

Equation 5: Generalized Monod Kinetics

Where I_n represents some inhibition function.

Various inhibitory effects come into play in waste water treatment processes, which further complicate the modelling of an already highly interdependent system. The most commonly modelled inhibitions are:

1) Competitive uptake inhibition

$$I = \frac{1}{1 + \frac{S_I}{S_j}}$$

Equation 6: Competitive Uptake Inhibition

Competitive uptake inhibition is prevalent in cases where a population of micro-organisms can metabolize a number of different substrates. In essence the substrates can be seen as competing for the attention of the micro-organisms. As the concentration of the competing inhibitory substrate (S_i) tends to zero, the inhibition function tends to unity (i.e. no inhibition). Whereas when the concentration of the competing substrate becomes large relative to the target substrate (S_j), the inhibition function tends to zero (i.e. complete inhibition).

2) Non-competitive inhibition

$$I = \frac{1}{1 + \frac{S_I}{K_I}}$$

Equation 7: Non-competitive Inhibition

This is where the existence of a different substrate in solution (which is metabolized by a different functional organism group altogether) inhibits the uptake of the target substrate.

3) pH inhibition

$$I_{pHZ_j} = \frac{1 + 10^{pHj(pH_{LLZj} - pH_{ULZj})}}{1 + 10^{(pH_r - pH_{ULZj})} + 10^{(pH_{LLZj} - pH_r)}}$$

Equation 8: pH Inhibition

Where

I_{pHZj} = pH inhibition function of functional organism group j

pH_{ULZj} = Upper pH level of 50% inhibition

pH_{LLZj} = Lower pH level of 50% inhibition

pH_r = Reactor pH

pH_j = pH inhibition constant

The abovementioned pH inhibition function is described as a two-sided empirical formulation. In AD-FTRW1, pH inhibition is applied in this form to all trophic groups. The inhibition function is a "bell-shaped" curve distributed about a specified average (the arithmetic mean of the upper and lower pH limits) that ranges from zero (complete inhibition) to 1 (no inhibition) (van Zyl 2008).

4) Temperature inhibition

Temperature is highly influential on functional organism group activity. For mesophilic anaerobic digestion (which operates around 37°C), a deviation of 5°C in either direction can lead to catastrophic failure of the digester. The temperature inhibition function applied to all Functional Organism Groups[2] (FOG's) in AD-FTRW1 is displayed below:

$$I_T = \frac{1 + 10^{T_j(T_{LL} - T_{UL})}}{1 + 10^{(T_r - T_{UL})} + 10^{(T_{LL} - T_r)}}$$

Equation 9: Temperature Inhibition

Where:

I_T = Temperature inhibition function
T_r = Reactor temperature (Kelvin)
T_j = Temperature inhibition constant
T_{UL} = Upper temperature at which 50% inhibition is experienced (Kelvin)
T_{LL} = Upper temperature at which 50% inhibition is experienced (Kelvin)

5) Dissolved hydrogen inhibition

Dissolved hydrogen gas is the most inhibitory metabolic intermediate in anaerobic digestion. Even at very low concentrations, dissolved hydrogen gas inhibits the activity of the hydrogen producing micro-organisms; specifically acidogens and acetogens. Propionate reducing acetogens are especially sensitive to dissolved hydrogen gas concentration. One such inhibition function for acidogenesis is as follows:

$$I_{H_2 Z_{ad}} = 1 - \frac{[H_{2(aq)}]}{k_{I.H_2 Z_{ad}} + [H_{2(aq)}]}$$

Equation 10: Dissolved hydrogen inhibition

Where:

$[H_{2(aq)}]$ = the dissolved hydrogen concentration (mg/l)

$k_{I.H_2 Z_{ad}}$ = hydrogen inhibition constant (mg/l)

(Sotemann et al., 2006)

[2] A Functional Organism Group is defined as a population of micro-organisms within a culture that are responsible for degrading a specific substrate within a specific process in anaerobic degradation e.g hexanoic acid acetogenesis.

Other dissolved hydrogen inhibition functions have been proposed to represent inhibition of acetogens and can be found in the literature of Batstone et al. (2002).

6) SCFA inhibition

Finally, the total SCFA concentration in the reactor can reach inhibitory levels; especially for acetoclastic methanogens and the propionate reducing acetogens. An appropriate inhibitory function for the modelling of this phenomenon is:

$$I_{AZj} = \frac{1}{\left[1 + \frac{[SCFA_e]}{k_{AZj}}\right]}$$

Equation 11: SCFA inhibition

Where:

$[SCFA_e]$ = Total SCFA concentration in the reactor (mg/l)

k_{AZj} = Inhibition constant (mg/l)

c. *Physico-chemical process implementation*

Ultimately, an AD model consists of biological reactions which are slow (time constants of the order of days and hours) and physico-chemical reactions which are comparatively rapid (time constants of the order of seconds and milliseconds). This results in a system of differential equations described as stiff (due to the large range of time constants) and introduces complications in the solution of the system of equations. The problem is that most numerical integrators for systems of differential equations determine the maximum step size with respect to time that will maintain a specified degree of accuracy in the solution. This determination is usually based on relative derivative magnitudes for the variables involved in the system of equations. The size of an integration time step in a stiff system is thereby limited by the time constants of the rapid reactions which result in large time derivatives for their associated variables. In waste water treatment where hydraulic retention times (based on biological reaction rate constants) are typically in the order of days resulting in simulations of similar magnitudes, these large time derivatives cause integrators to increment in the order of seconds and milliseconds resulting in computationally long and intensive simulations that are impractical.

In order to bypass this problem, the approach is to treat the rapid physico-chemical reactions as equilibrium reactions such that they can be described as algebraic equations. This greatly simplifies the solution of the system of equations. The motivation for this approach is that, from the slower reaction's perspective, the faster reactions can be considered instantaneous and be assumed to always reach equilibrium before the slower reactions terminate for each time step (Rosen et al., 2005). One is then left with a system of differential and algebraic equations (DAE) which can be solved more easily than the stiff set of differential equations (Batstone et al., 2002).

2.5.3 *AD-FTRW1*

AD-FTRW1 was developed in 2008 by Dr Pierrie Van Zyl as part of his PhD thesis under the supervision of Professor George Ekama and Professor Mark Wentzel. The research was carried out at the University of Cape Town's Water Research Group and the thesis (entitled Anaerobic Digestion of Fischer-Tropsch Reaction Water) focussed on the design, construction, performance evaluation and modelling of a lab-scale submerged membrane anaerobic bioreactor.

The model that was developed, referred to as AD-FTRW1, combines COD balances, mass balances, proton balances (for pH prediction) and component balances through stoichiometric relations and organism growth and death functions in order to describe the complex process of anaerobic digestion of Fischer-Tropsch reaction water under dynamic and steady-state conditions (van Zyl 2008).

The approach was to define various Functional Organism Groups (FOG) responsible for acidogenesis, acetogenesis of each SCFA or alcohol that is available in significant proportions in Fischer-Tropsch reaction water and Functional Organism Groups responsible for the methanogenic processes. The significant short chain fatty acids and other components include acetic acid, propanoic acid, butanoic acid, valeric acid, hexanoic acid, ethanol and methanol.

The biological part of the model describes acidogenesis, acetogenesis and methanogenesis. Significantly the only necessary hydrolysis steps are the hydrolysis of urea (which is dosed to provide the N requirements of the biomass) and the hydrolysis of inactive endogenous mass. Other than this, there is no other hydrolysis taking place as the influent stream only consists of SCFAs and alcohols which are already in a soluble form and amenable to either acetogenesis or methanogenesis (van Zyl 2008).

AD-FTRW1 also represents inter-phase mass transfer in terms of carbon dioxide expulsion/dissolution and the weak acid-base system of inorganic carbon, albeit in a simplified manner.

Biological kinetics include inhibitory effects of temperature, pH, dissolved hydrogen concentration and SCFA concentration. Specific growth rate is described via Monod kinetics.

Figure 5 presents a schematic outlining the dynamic model metabolic pathways and functional organism groups. Sections 2.5.3 (a-c) describe Bioprocesses, Aqueous Chemical Processes and Physical Processes used in AD-FTRW1 in more detail.

a. ***Bioprocesses***

i. **Conceptual Model**

As with several bioprocess models, the biomass was classified (according to the transformations that it mediates) into the four traditional trophic groups in anaerobic digestion namely acetogens (Z_{ac}), acetoclastic methanogens (Z_{am}), hydrogenotrophic methanogens (Z_{hm}) and acidogens (Z_{ad}) (Figure 5). However, to compensate for the range of SCFAs and alcohols in the feed, a specific FOG was assigned to each substrate (van

Zyl 2008). Similar to Sotemann et al. (2005) an endogenous death process was included in the model for each FOG. Along with unique growth and death rates and substrate utilization capabilities, the FOGs are allowed to respond differently to substrate concentrations and environmental conditions.

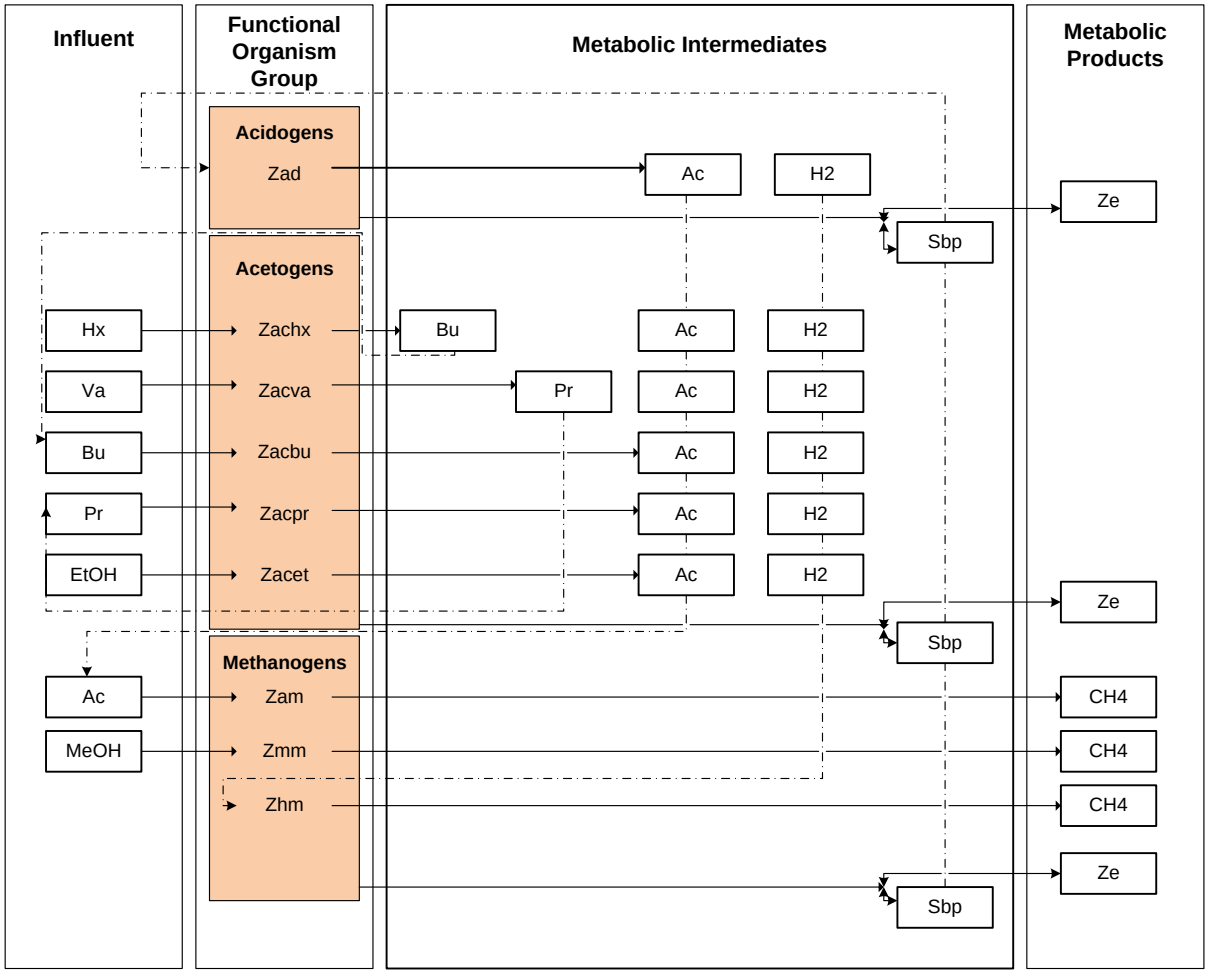

Figure 5: Schematic of Conceptual Model

Figure 5 depicts the influent characterization, metabolic pathways and Functional Organism Groups of the dynamic model (van Zyl 2008).

The development of the conceptual model was further based on the following assumptions (van Zyl 2008):

1) All the biomass had an elemental composition of $C_5H_7O_2N$ (McCarty 1975).
2) All CO_2 produced metabolically would be in soluble form (H_2CO_3) thus:

$$CO_{2\,\mathrm{Produced}} + H_2O \rightarrow H_2CO_3$$

3) The contribution of CO_3^{2-} to the total carbonate was regarded as negligible in the anaerobic digestion pH range of 6.5 – 7.5.

4) Only the protonated (non-ionic) form of any SCFA can be metabolized, thus un-protonated (ionic) SCFAs need to pick up a proton from a weak acid/base system before metabolism. The fraction of the SCFA in the un-protonated form was assumed to be governed by the influent pH.

$$C_x H_{y-1} O_2^- + H_2CO_3 \rightarrow C_x H_y O_2 + HCO_3^-$$

5) Urea was the sole nitrogen source for AD-FTRW and was dosed into the reactor feedstock. In the operational pH range (6.5-7.5) >99% of the ammonia will be in protonated (NH_4^+) form. Thus upon entering the reactor urea decomposes rapidly to form protonated ammonia in urea hydrolysis.
6) Similarly, it was assumed that the NaOH dosed for pH control is converted to carbonate alkalinity upon entering the system. Under normal operating conditions, the carbonate system (HCO_3^-/H_2CO_3) concentration is significantly (10 times) larger than any other weak acid/base concentration; it was assumed that this system would serve as the primary proton source/sink.

Both assumptions 5 and 6 were confirmed experimentally (van Zyl 2008). The assumptions made above were applied in conjunction with the metabolic pathways to derive the dynamic AD-FTRW1 model stoichiometry.

ii. **Stoichiometry**

This section focuses on the reaction stoichiometry of AD-FTRW1. Reactions include hydrolysis and acidogenesis of dead endogenous mass, acetogenesis of SCFAs, methanol methanogenesis, acetoclastic methanogenesis, hydrogenotrophic methanogenesis, urea hydrolysis, CO_2 expulsion/dissolution and conversion of hydroxide to carbonate.

For each biologically mediated reaction, a functional organism group is represented and the growth and death of these groups is incorporated. For the sake of brevity, only the overall metabolic reactions of the biological reactions and stoichiometry thereof will be reviewed here.

This section deals with the conversion of the different substrates by each of the FOGs to metabolic end products resulting in biomass growth. Associated with each of the 9 growth processes is a corresponding death process.

The derivation of the bioprocess stoichiometry of AD-FTRW1 followed the basic approach of Sötemann et al. (2005). The catabolic pathways of the individual SCFAs, MeOH, EtOH and the slowly biodegradable organics (S_{bp}) produced by anaerobic biomass death and hydrolysis were obtained from literature (Kalyuznhyi, 1997b; McCarty, 1975; Batstone et al., 2002; Sötemann et al., 2005). Some of the weak acid-base chemistry (WABC) relationships for the system were incorporated into the stoichiometry of each organism group, to reduce the stiffness of the system of differential equations and thus computation time. The derivation was extended through the integration of ionic speciation (of the carbonate and acid systems) into the bioprocess stoichiometry. This process was guided by model assumptions 2, 3, 4 and 6 above (van Zyl 2008).

The death processes follow the theory laid out by Dold et al. (1980) on endogenous respiration. This theory states that organism growth and death happen concurrently at a continuous rate. The ‘dead biomass’ is then

classified into two fractions; its unbiodegradable fraction (f) and its biodegradable fraction (1-f). The unbiodegradable fraction is known as endogenous residue (Z_e) while the other fraction is referred to as biodegradable particulate (S_{bp}) and is hydrolyzed to form substrate for acidogenesis. Traditionally hydrolysis and acidogenesis are modeled as two separate processes in anaerobic digestion (Batstone et al., 2002 & Sötemann et al., 2005). However in AD-FTRW1, the only biodegradable particulates (S_{bp}) that enter the system are those produced from dead organism mass (van Zyl 2008). It is therefore assumed that S_{bp} has the same composition as that of active biomass i.e. $C_5H_7O_2N$. The contribution of this organism group is so small that it was decided to model both hydrolysis and acidification in a single step (Process 1 in Figure 16).

The stoichiometry of each of the bioprocesses represented in AD-FTRW1 is reviewed in detail in the sub-sections that follow.

2.5.3.a.ii.1 Acetogenesis of Short Chain Fatty Acids and Ethanol

$$(1-F)C_xH_{2x}O_z + F.C_xH_{(2x-1)}O^- + \left[E\left[\frac{5.D_s}{20} - x\right] + F - \left[\frac{E.D_s}{20}\right]\right].H_2CO_3 + \left[(1-E)(2-z+2p) - E\left[\left[\frac{8.D_s}{20}\right] - (2x-z)\right] - E\left[\left[\frac{5.D_s}{20}\right] - x\right]\right].H_2O + \frac{E.D_s}{20}NH_4^+ \xrightarrow{r_{ac}} (1-E)C_2H_4O_2 + (1-E)C_{xp}H_{ypq}O_2 + (1-E)\left[x + 2p - z - \left[q.z\left[\frac{x-2}{2}\right]\right]\right]H_2 + \left[F - \left[\frac{E.D_s}{20}\right]\right]HCO_3^- + \left[\frac{E.D_s}{20}\right]C_5H_7O_2N \quad \textit{(van Zyl 2008)}$$

Equation 12: AD-FTRW1's Acetogenesis of Short Chain Fatty Acids and Ethanol

Where:

F is the fraction of organic acid in dissociated form

D_s is the electron donating capacity of the substrate

E is the fraction of biodegradable COD that is converted to biomass

And

If $\frac{x}{3} \geq 1\ then\ p = 1 \quad else \quad p = 0$

If $x = 3\ then\ q = 0\ else\ q = 1$

Note that the above generic equation includes the incorporation of weak acid base chemistry relationships of SCFA dissociation, inorganic carbon speciation and dissolved ammonia speciation as they are represented in the model.

2.5.3.a.ii.2 Acetoclastic Methanogenesis

$$\frac{5(1-F_{ac})}{2.Y_{am}}C_2H_40_2 + \frac{5F_{ac}}{2Y_{am}}C_2H_3O_2^- + NH_4^+ + \frac{(5-11Y_{am})}{2Y_{am}}H_2O + \frac{(5-3Y_{am}-5F_{ac})}{2Y_{am}}H_2CO_3 \xrightarrow{r_{am}} \frac{(5-5Y_{am})}{2Y_{am}}CH_4 + \frac{(5-2Y_{am})}{2Y_{am}}HCO_3^- + C_5H_7O_2N$$ (van Zyl 2008)

Equation 13: AD-FTRW1's Acetoclastic Methanogenesis

Where Y_{am} is the true organism yield.

Acetoclastic methanogens, together with acetogens, are the most prominent organisms in the anaerobic digestion of FTRW.

2.5.3.a.ii.3 Hydrogenotrophic methanogenesis

$$\frac{10}{7Y_{hm}}H_2 + NH_4^+ + HCO_3^- + \frac{10(5-3Y_{hm})}{20Y_{hm}}H_2CO_3 \xrightarrow{r_{hm}} \frac{10(1-Y_{am})}{4Y_{am}}CH_4 + \frac{10(15+11Y_{am})}{20Y_{am}}H_2O + Z_{hm}$$

(van Zyl 2008)

Equation 14: AD-FTRW1's Hydrogenotrophic Methanogenesis

Where Z_{hm} refers to one mole of biomass, and is also represented by the stoichiometric formula of $C_5H_7O_2N$.

2.5.3.a.ii.4 Methanogenesis of methanol

$$\frac{10}{3Y_{mm}}CH_3OH + NH_4^+ + HCO_3^- \xrightarrow{r_{mm}} \frac{30(1-Y_{am})}{12Y_{am}}CH_4 + \frac{(5-9Y_{mm})}{6Y_{mm}}H_2CO_3 + \frac{(5+33Y_{mm})}{6Y_{mm}}H_2O + C_5H_7O_2N$$

(van Zyl 2008)

Equation 15: AD-FTRW1's Methanogenesis of Methanol

2.5.3.a.ii.5 Hydrolysis and Acidogenesis

$$\frac{1}{Y_{ad}}C_5H_7O_2N^{dead} + \frac{5(1-Y_{ad})}{Y_{ad}}H_2O \xrightarrow{r_{ad}} \frac{2(1-Y_{ad})}{Y_{ad}}C_2H_4O_2 + \frac{2(1+Y_{ad})}{Y_{ad}}H_2 + \frac{(1-Y_{ad})}{Y_{ad}}HCO_3^- + \frac{(1-Y_{ad})}{Y_{ad}}NH_4^+ + C_5H_7O_2N^{active}$$

(van Zyl 2008)

Equation 16: AD-FTRW1's Hydrolysis and Acidogenesis

Acidogenic bacteria are present in significantly reduced concentrations in the anaerobic digestion of FTRW. This is due to the fact that the influent organics are already predominantly in a soluble form and therefore the role of the acidogens in this context is only to hydrolyze dead biomass.

2.5.3.a.ii.6 Organism death

The death process for each FOG is described by the following stoichiometry:

$$Z_{xx} \xrightarrow{r_e} (1-f).S_{bp} + f.Z_e$$

Equation 17: AD-FTRW1's Organism Death

Where the "xx" subscript is adopted to denote the biomass of each FOG separately and so can take on the following labels explained in the LIST OF ACRONYMS/A: ad, acHx, acVa, acBu, acPr, acEt, mm, am and hm.

iii. **Process Kinetics (Uptake, Death and Inhibition)**

2.5.3.a.iii.1 Uptake Kinetics

AD-FTRW1 adopts Monod kinetics to describe substrate uptake.

2.5.3.a.iii.2 Inhibition Kinetics

During the development of AD-FTRW1 the most significant inhibitory effects were deemed to be caused by temperature fluctuations, pH deviations, as well as by abnormal dissolved hydrogen and SCFA concentrations. Below is a summary of the inhibition functions included in the bioprocess kinetics of AD-FTRW1.

$$r_j = \frac{\mu_{\max\ j} S_j}{(K_{sj} + S_j)} Z_{Aj}.I_T.I_{pH}I_{H_2}I_{SCFA}$$

Equation 18: Typical abbreviated rate expression in AD-FTRW1

A full representation of the uptake kinetics for AD-FTRW1 with all inhibitory functions included reads as follows:

$$r_j = \frac{\mu_{\max\ j} S_j}{(K_{sj} + S_j)} Z_j.\left(\frac{1 + 10^{-0.5(T_{UL} - T_{LL})}}{1 + 10^{(T_r - T_{UL})} + 10^{(T_{LL} - T_r)}}\right).\left(\frac{1 + 10^{pHj(pH_{LLZj} - pH_{ULZj})}}{1 + 10^{(pH_r - pH_{ULZj})} + 10^{(pH_{LLZj} - pH_r)}}\right).\left(\frac{1}{1 + \frac{[H_2]}{k_{IH2Zj}}}\right).\left(\frac{1}{\left[1 + \frac{[SCFA]}{k_{AZj}}\right]}\right)$$

Equation 19: Typical comprehensive rate expression in AD-FTRW1

In AD-FTRW1 it was decided not to include all forms (Temperature, pH, $[H_2]$ and [SCFA]) of inhibition for all FOGs since certain inhibitions are only applicable to certain FOGS. The kinetics, as applied in AD-FTRW1, can be seen in Table 4 on the following page. The functions and their corresponding inhibition parameters were obtained from the literature and are presented in Table 5.

Table 4: Bioprocess inhibitions

No:	*Process Code*	*Process Description*	*Active Inhibitions*			
			I_T	I_{pH}	I_{H_2}	I_{SCFA}
1	*ad*	Hydrolysis and Acidogenesis of Sbp	✓	✓	✓	✗
3	*acHx*	Hexanoic Acid Acetogenesis	✓	✓	✓	✗
5	*acVa*	Valeric Acid Acetogenesis	✓	✓	✓	✗
7	*acBu*	Butyric Acid Acetogenesis	✓	✓	✓	✗
9	*acPr*	Propionic Acid Acetogenesis	✓	✓	✓	✓
11	*acEt*	Ethanol Acetogenesis	✓	✓	✓	✗
13	*mm*	Methanol Methanogenesis	✓	✓	✗	✗
15	*am*	Acetoclastic Methanogenesis	✓	✓	✗	✗
17	*hm*	Hydrogenotrophic Methanogenesis	✓	✓	✓	✗

Some reasoning for the varying application of inhibitions in the biological processes is supplied in section 2.5.2b.ii. Importantly pH and temperature inhibition is applicable to all FOGs.

Table 5: Inhibition Function Constants

Dissolved Hydrogen Concentration		
k_{IH_2Zad} *(mol/l)*	6.25E-04	
k_{IH_2Zac} *(mol/l)*	1.00E-05	
k_{IH_2ZacPr} *(mol/l)*	3.50E-06	
Total SCFA Concentration		
$k_{IAtZacPr}$ *(mol/l)*	0.018	
k_{IAtZam} *(mol/l)*	0.1	
Temperature	***Lower Limit (LL)***	***Upper Limit (UL)***
T (K)	305	315
pH	***Lower Limit (LL)***	***Upper Limit (UL)***
pH_{ZadZac}	4	8
pH_{ZamZmm}	6.5	8
pH_{Zhm}	6.5	8

Van Zyl (2008)

2.5.3.a.iii.3 Death Kinetics

In AD-FTRW1, death kinetics followed the theory of Dold et al. (1980). The reaction rate was simply described in terms of first order kinetics as follows.

$$r = b[Z_{xx}]$$

Equation 20: AD-FTRW1's death kinetics

b. ***Aqueous Chemical Processes***

AD-FTRW1 uses a simplification of the approach developed by Musvoto et al. (2000) in order to represent ionic speciation. An approximate representation of the dominant weak acid-base systems (the carbonate, ammonia and organic acid systems), was derived for a limited pH range (6.5 – 7.5) and embedded into the stoichiometry of the biological reactions. The assumption that the pH will remain in this range is the major limitation of AD-FTRW1.

2.5.3.b.i.1 WABC/Ionic speciation

SCFA speciation/dissociation was assumed to be governed by the pH of the feed stream and is implemented in the model via the F parameter which is the fraction of a specific SCFA in dissociated form. Each of the SCFA's has an individual pK_a value and the associated F value is calculated as follows:

$$F_{C_x} = \frac{C_xH_{2x-1}O_2^-}{(C_xH_{2x-1}O_2^- + C_xH_{2x}O_2)} = \frac{1}{\left(1+\frac{[H^+]_{feed}}{K_{ax}}\right)}$$

Equation 21: Fraction of SCFA in dissociated form

where

x = 1 to 6

$K_{ax} = 10^{-pKax}$ of the SCFA with carbon chain length x

$[H^+]_{feed}$= Feed proton activity = $10^{-pHfeed}$

For the inorganic carbon weak acid-base system, the contribution of CO_3^{2-} was regarded as negligible in the anaerobic digestion pH range (pH 6.5 - 7.5) as outlined in assumption 3 in section 2.5.3a.i above. Instead HCO_3^- was used in the stoichiometry as the dominant inorganic carbon species.

Both SCFA speciation/dissociation and the inorganic carbon WABC are embedded into the bioprocess stoichiometry via the F parameter and HCO_3^- respectively.

The only weak acid/base chemistry relationships not embedded in the metabolic processes are the conversion of hydroxide (OH^-) to bicarbonate (HCO_3^-) and the expulsion/dissolution of carbon dioxide (also classified as a physical process below).

The conversion of hydroxide to bicarbonate is associated with NaOH dosage in the actual reactor system. It is necessary to convert hydroxide alkalinity into carbonate alkalinity such that the model can interpret the dosage.

$$NaOH + H_2CO_3 \rightarrow Na^+ + H_2O + HCO_3^-$$

Equation 22: Conversion of Hydroxide to Bicarbonate

The micro-organisms which mediate anaerobic digestion are highly pH sensitive. FTRW needs to be dosed with an alkaline cocktail in order to control the pH level in the digester and enhance micro-organism activity.

The final process in AD-FTRW1 describes the hydrolysis of urea to saline ammonia.

$$(NH_2)_2CO + 2H_2CO_3 + H_2O \rightarrow CO_2 + 2NH_4^+ + 2HCO_3^-$$

Equation 23: Urea hydrolysis

Both of these process rates (hydroxide to bicarbonate and urea hydrolysis) were implemented with first order kinetics dependent on the significant reactant in each; hydroxide and urea respectively. The first order kinetics are depicted below for clarity;

$$r_x = K_x[X]$$

Equation 24: First order kinetics

Where the "x" represents either hydroxide or urea (depending on which reaction is being referred to) and K_x represents the appropriate rate constant.

2.5.3.b.i.2 pH calculation

pH (in AD-FTRW1) is calculated according to the following formula:

$$pH = -\log\left[\frac{K_h + \left(K_h^2 - 8\left(\frac{C_t}{K_{c1}P_{CO2}} - 1\right)K_{c2}\right)^{\frac{1}{2}}}{2\left(\frac{C_t}{K_{c1}P_{CO2}} - 1\right)}\right]$$

where;

K_h is Henry's law constant

P_{CO2} is the partial pressure of carbon dioxide

C_t is the total concentration of inorganic carbon

K_{c1} is the first dissociation constant of carbonic acid

and K_{c2} is the second dissociation constant of carbonic acid

The pH calculation scheme is based on an inorganic carbon balance, coupled with equilibrium relationships for 1st and 2nd dissociation and carbon dioxide expulsion. The calculation uses the bicarbonate concentration as an approximation for the total inorganic carbon concentration. While this approximation is effective in the pH range of 6.5 – 7.5 where bicarbonate is the dominant inorganic carbon species, the approximation is invalid outside of this range.

c. ***Physical Processes***

2.5.3.c.i.1 Gas Exchange

The process of carbon dioxide expulsion/dissolution is represented in AD-FTRW1. Various authors (including Rosen et al., 2005) suggested that the forward and reverse reaction can be described by a single equilibrium reaction. The formulation, as it is applied in the model, is presented below:

$$H_2CO_3^* \xrightarrow{r_{eqCO2}} CO_{2(g)} + H_2O$$

Equation 25: Carbon dioxide expulsion/dissolution

Where

$r_{eqCO2} = r_{fCO2} - r_{rCO2} = K_{fCO2}[H_2CO_3^*] - K_{rCO2}[CO_{2(g)}]$

or

$$r_{eqCO2} = K_{fCO2}\left(\left[H_2CO_3\right] - K_{eqCO2}\left[CO_{2(g)}\right]\right)$$

Where

$K_{eqCO2} = \frac{K_{rCO2}}{K_{fCO2}} = \frac{R.T_k}{K_h}$ = CO_2 Equilibrium Constant [dimensionless]

K_h = Henry's Law Constant [L.atm.mol^{-1}]

R = Ideal Gas Law Constant [L.atm.(mol.K)$^{-1}$]

T_k = Temperature [Kelvin]

K_{fCO2} = CO_2 kinetic constant [1/d]

2.5.4 *UKZN's Ionic Speciation model*

Speciation refers to the detailed distribution of total chemical species concentrations between the ionic species that exist in their associated weak acid/base systems. The Pollution Research Group at the University of Kwa-Zulu Natal (through collaboration with UCT's Water Research Group) has developed an external equilibrium speciation model that handles aqueous phase ionic equilibria (weak acid-base chemistry) and ionic pairing that is compatible with UCT wastewater treatment models (Brouckaert et al., 2010). The ionic speciation model is based on acid-base chemistry and dissolved inorganic carbon chemistry as laid out by Stumm and Morgan (1995). As Sasol Technology's Biological model of Anaerobic Digestion (AD-FTRW1) has adopted the UCT approach to waste water treatment modelling, there is significant scope for the integration of this Ionic Speciation model with AD-FTRW1.

The ionic speciation model can be described as an aqueous phase, weak acid/base, solution chemistry model dealing with the inorganic carbon, ammonia, acetate and phosphate systems. It has formed an integral part in the extension of UCTADM1 to a 3-phase UCTAD model which incorporates a phenomenon that was previously unrepresented; mineral precipitation. However precipitation reactions are probably not significant in the Anaerobic Digestion of FTRW.

The interfacing of the ionic speciation model with the biological model is achieved via total component concentrations. The reason for this is that total component concentrations are conserved quantities in material balance calculations. The ionic components represented in UCT's 3 phase AD biological model are H^+, Na^+, K^+, Ca^{++}, Mg^{++}, NH_4^+, Cl^-, Ac^-, Pr^-, $SO_4^=$, $CO_3^=$ and $PO_4^{-=}$ and represent the total concentrations of the weak acid/base systems concerned. These total concentrations are then speciated into 42 corresponding ionic species via the ionic speciation model from which significant process variables such as free and saline ammonia (NH_3+NH_4^+: FSA) released, bicarbonate alkalinity and digester pH can be calculated.

Studies have shown that ionic speciation reactions in the aqueous phase, as compared to biological and inter-phase reactions are orders of magnitude faster. For this reason, they can be considered to be at equilibrium at all times and they are implemented as such. This divides an AD model (consisting of relevant biological and physico-chemical processes) into differential mass balances, which determine the compositions in terms of total concentrations, followed by an algebraic equilibrium speciation calculation, which determines the detailed ionic composition at each time step. On the following page is an example of equilibrium and mass balance equations for ionic speciation.

Table 6: Example of Equilibrium and Mass Balance Equations for Ionic Speciation.

Weak Acid Sub-system	*Aqueous phase equilibrium equations*	*Mass Balance Equations*
Ammonia	$\{NH_3\} = \frac{K_{NH_4}.\{NH_4^+\}}{\{H^+\}}$ $\{NH_4SO_4^-\} = \frac{\{SO_4^{2-}\}\{NH_4^+\}}{K_{NH_4SO_4}}$	$N_t = [NH_4^+] + [NH_3] + [NH_4SO_4^-]$

(Loewenthal et al., 1989)

As can be seen in the above table, the total concentration (N_t) of an aqueous ionic system is the sum of the sub-species making up that system. These total concentrations (N_t) can be calculated through the differential mass balance relationships in the biological model. Equilibrium relationships as depicted in column 2 above can then be used in order to determine in what proportions the total ionic system concentration speciates into its constituents sub-species. Reliable values for equilibrium partition co-efficients K_i are presented in the literature for practically all weak acid/base sub-systems of interest in anaerobic digestion modelling.

The speciation of the total components into their constituent sub-species is achieved via an iterative, numerical procedure that accounts for non-idealities in solution via activities. The activity of a dissolved species is a measure of its effective concentration in solution and is calculated as a product of its concentration and a species specific activity co-efficient as is depicted below for NH_4^+.

$$\{NH_4^+\} = \gamma_{NH_4^+}[NH_4^+]$$

Equation 26: Activity calculation

where;

$\{NH_4^+\}$: activity of NH

$\gamma_{NH_4^+}$: activity coefficient of NH

$[NH_4^+]$: concentration of NH

The activity co-efficient is largely a function of temperature and the ionic strength of solution. Debye and Huckel developed a theory with which single ion activity coefficients could be calculated on the basis of electrostatic interactions between ions and their thermal motion in solution. It must be noted that single ion activity coefficients are a calculational construct as an anion can never exist independently in solution but rather is always accompanied by its associated cation. For this reason activity coefficients of single ions cannot be measured and therefore the Debye-Huckel theory calculates mean activity coefficients for a cation/anion pair and therewith allocates single ion activity coefficients on the basis of ionic charge. The use of single-ion activity coefficients greatly simplifies calculations (Stumm and Morgan 1995).

$$-\log\gamma_i = \frac{Az_i^2\mu^{\frac{1}{2}}}{1 + Ba\mu^{\frac{1}{2}}}$$

Equation 27: Extended Debye-Huckel Equation

Where:

$\mathrm{A} = 1.82 \times 10^6(\in \mathrm{T})^{\frac{-3}{2}}$

$\mathrm{B} = 50.3(\in \mathrm{T})^{\frac{-1}{2}}$

And

a : an adjustable parameter corresponding to the size of the ion in angstroms

$\in$: dielectric constant of the solvent

z_i : the charge of ionic species i

An important parameter to take note of in Equation 27 above is the ionic strength of solution denoted μ. According to Stumm and Morgan (1995), "Ionic strength is a measure of the interionic effect resulting primarily from electrical attractions and repulsions between the various ions in solution." It is defined by the following equation that sums the product of charge and concentration over all anions and cations in solution.

$$\mu = \frac{1}{2}\sum C_i z_i^2$$

Equation 28: Ionic strength of solution

UKZN's ionic speciation routine does not however make use of the extended Debye-Huckel equation to calculate activity co-efficients due its limited applicability ($\mu < 10^{-2.3}\ M$). Instead the routine makes use of the Davies equation which is more accurate at higher concentrations ($\mu < 0.5\ M$). The Davies equation is an empirical extension of the Debye-Huckel theory and is depicted below.

$$-\log\gamma_i = Az_i^2\left(\frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - 0.2\mu\right)$$

Equation 29: Davies Equation

The speciation routine also takes into account the temperature dependency of equilibrium constants with use of the Van't Hoff equation depicted below.

$$\frac{d \ln K}{dT} = \frac{\Delta H^o}{RT^2}$$

Equation 30: Van't Hoff Equation

Reference equilibrium constants (K_{ref}) and standard enthalpies of reaction (ΔH^0) used in the Brouckaert et al. (2010) subroutine were sourced from the MinteqA2 database.

2.5.5 *WEST*

Modelling was performed using the WEST software version 3.7.6. WEST is an open source waste water treatment modelling software with built in differential and algebraic equation solvers. The software consists of three platforms; the model editor, the configuration builder and the experimental environment (Vanhooren et al., 2003).

Reactor models are conveniently programmed via the model editor interface presented as a Gujer Matrix. This makes modelling much faster as the programme is designed to generate the necessary model code (msl files) from what is specified in the Gujer matrix. The Gujer matrix is a structured representation of reactions (presented in each row), components (presented in each column) and reaction rates (presented in the final column) that are involved in a reactor model (Vanhooren et al., 2003).

The configuration builder, allows the modeller to set up various process configurations that call on different models for each unit operation in the process. The software generates unique code for each configuration built in this platform and these process models are then executed in the experimentation environment. The dedicated code generators help enhance computational speed in the experimentation environment.

The experimentation environment allows for high-end analysis such as process simulation, parameter estimation and sensitivity analysis (Vanhooren et al., 2003). Systems of differential and algebraic equations are solved using a selection of numerical integrators.

2.6 Model Evaluation

Statistical model evaluation forms an important part of model validation. The performance of models is generally evaluated subjectively by human perceptions of how closely the model fits experimental data in the context of graphical representations (Schunn et al., 2005). The wastewater treatment modelling field is no exception where literature reveals that evaluation of model quality is often based on qualitative comparisons between modelled and observed outputs (Hauduc et al., 2011). These subjective evaluations can be unreliable or misleading and it is advisable to adopt an objective statistical approach to model evaluation. A quantitative approach is not only preferable since it eliminates the existence of human bias in model evaluation but also

because it enables the development of automatic calibration and evaluation procedures (Hauduc et al., 2011). The approach should consider the trade-off between model complexity and model accuracy with the golden aim of achieving the least complex, most accurate model possible (Dochain and Vanrolleghem 2001). The purpose of this section is to review different methods of model evaluation with a view to selecting a model evaluation approach that is applicable to AD-FTRW2.

In evaluating candidate models one can adopt two approaches to assess their effectiveness in representing data; goodness-of-fit tests or structure characterization methods.

2.6.1 *Structure Characterization*

Dochain and Vanrolleghem (2001) describe structure characterization as the process of selecting the best model structure among different model structure candidates on the basis of experimental data. Every process model contains two types of error; bias error which is the error introduced by the departure of the candidate model from the true underlying model, and variance error, which is caused by the candidate model's description of noise in the limited dataset used for system identification. In model building the aim is to minimize model error; the sum of bias error and variance error. Bias error tends to decrease with increasing model parameters (p) while variance error tends to increase with increasing p and decrease with increasing data points (N). In this way model's are simultaneously penalized for increased complexity and rewarded for increased accuracy and the structure characterization process guides the modeller toward the least complex, most accurate model that was alluded to earlier as the golden aim. It must be noted that the number of parameters in a model (p) gives a direct measure of model complexity.

Structure characterization methods can be divided into two categories; "a posteriori" structure characterization methods and "a priori" structure characterization methods (Dochain and Vanrolleghem 2001). "A posteriori" structure characterization methods assess the quality of different model structures once each model has been fitted to the data while "a priori" structure characterization methods are capable of differentiating between candidate model structures before parameter estimation has taken place. Generally applicable "a priori" structure characterization methods include utilizing the pattern recognition capabilities of neural networks and Numerical Algorithms for Subspace State Space System Identification (N4SID) (Dochain and Vanrolleghem 2001). This research aims to develop on an existing Anaerobic Digestion of Fischer-Tropsch Reaction Water Model (AD-FTRW1) and, for this reason and due to its complexity it appears that "a priori" structure characterization methods will not be applicable. For this reason, "a posteriori" structure characterization methods will be reviewed in more detail.

Various "a posteriori" structure characterization methods consist of criteria that include accuracy and complexity terms (such as the Final Prediction Error, Akaike's Information Criterion and the Bayesion Information Criterion), criteria that assess undermodelling (such as the General Information Criterion), statistical hypothesis tests (such as the F-test) and Diagnostic Checking (also known as analysis of residuals) (Dochain and Vanrolleghem 2001).

The criteria based methods allow for model selection via the philosophy that the model with the smallest criterion value should be selected. Expressions for the calculation of the Final Prediction Error and Akaike's Information Criterion are depicted below.

$$\frac{SSR}{N}\left[1+\frac{2p}{N-p}\right]$$

Equation 31: Final Prediction Error Criterion

$$N\log\left(\frac{SSR}{N}\right)+2p$$

Equation 32: Akaike's Information Criterion

Where:

N： number of data points

p： Number of parameters

SSR： sum of squared residuals $= \sum_{i=1}^{N}\left(y_i - f(x_i)\right)^2$

y_i： the i^{th} experimental point or variable to be predicted

$f(x_i)$： the model predicted variable

It is clear in the mathematical definition of the final prediction error that the index value increases with increasing p and decreases with increasing N and in so doing penalizes model complexity and rewards extensive model validation.

The F-test is one of the most frequently used statistical hypothesis tests to distinguish between various model structures.

$$\frac{(SSR_i - SSR_j)/(p_j - p_i)}{SSR_j/(N-p_j)}$$

Equation 33: F-test

The abovementioned test statistic (Equation 33) is compared with the F-distribution of characteristics $F(p_j - p_i, N - p_j)$ in order to decide whether the more complex model j provides a significantly (with a confidence level of α) better fit to an experimental data set than model i (Dochain and Vanrolleghem 2001). Literature suggests that in order to affect a meaningful comparison the ratio of data-points to parameters ($N:p$) should be at least of the order of 5:1 (Schunn et al., 2005).

Finally, diagnostic checking can be used as an "a posteriori" structure characterization method. This method, which is also referred to as the analysis of residuals, is based on the properties of the noise in the data. In most instances the noise (reflected by the prediction errors or residuals) is assumed to be an independent random variable. By using the auto-correlation or the run test, diagnostic checking can be used to evaluate the independence of the residuals. An outcome of dependence among the residuals translates into a conclusion that there are some un-modelled dynamics at play.

2.6.2 *Goodness-of-fit tests*

John von Neumann, one of the foremost mathematicians of the 20th century said, "With four parameters I can fit an elephant, and with five I can make him wiggle his trunk"(Dyson 2004). This quote helps to sum up the main problem with goodness-of-fit measures for model evaluation. The problem is that goodness-of-fit measures usually do not take into account model complexity via the number of free parameters (Schunn et al., 2005). It is therefore recommended that in conjunction with goodness of fit measures, researchers always divulge the number of free parameters in the underlying model together with the definition used to define a free parameter.

Numerical goodness-of-fit measures can be divided into two types; measures of deviation from exact data location (also referred to as absolute error) and measures of trend relative magnitudes (also referred to as correlation) (Schunn et al., 2005). The most frequently used measures of deviation from exact data location and trend relative magnitudes are root mean squared deviation (RMSD) and the coefficient of determination (r^2) respectively (Schunn et al., 2005). Legates and McCabe (1999) suggest that correlation measures should not solely be used to assess goodness-of-fit but that they should be coupled with summary statistics and absolute error measures (Legates and McCabe 1999). The calculational methods follow and variables, where not specified, take on the same meaning as was mentioned above in structure characterization.

$$RMSD = \sqrt{\frac{\sum_{i=1}^{N}(f(x_i) - y_i)^2}{N}}$$

Equation 34: Root mean squared deviation

As can be seen in the formulation of the root mean squared deviation (Schunn et al., 2005), the index gives a measure of the mean variance of model predictions about expected data. Via the squaring operation, the index penalizes poorly fitted data points more severely than closely fitted data points and also ensures that there is no error compensation caused by the summing of positive (over-prediction) and negative (under-prediction) errors.

The coefficient of determination (r^2) is more commonly applied to linear models. Evidence of its application to nonlinear models exists but for such cases the use of a pseudo-r^2 coefficient is recommended (Schunn et al., 2005). A general definition of the coefficient of determination is that it is the proportion of variability in the dataset that is accounted for by the model. Mathematically this translates into the definition which follows.

$$R^2 = 1 - \frac{SSR}{SST}$$

Equation 35: Coefficient of determination

Where:

$$\text{SST}: \text{ total sum of squares} = \sum_{i=1}^{N} (y_i - \bar{y})^2$$

$\bar{y}$: data mean

SSR : sum of squared residuals (as was previously defined)

AD models are highly non-linear which presents complications in applying the co-efficient of determination to evaluate model/data correlation.

Hauduc et al. (2011) suggests two other ways of classifying goodness-of-fit criteria. The first classification scheme characterizes the criteria according to their underlying mathematical structures into six classes; single event statistics, absolute criteria from residuals, residuals relative to observed values, total residuals relative to total observed values, agreement between distributional statistics of observed and modelled data, and comparison of residuals with reference values and with other models. The second classification scheme is based on the characteristic of the model that the criterion exposes namely mean error, bias, large errors, small errors, peak magnitude and chronology of events.

The abovementioned RMSD is an example of an absolute criterion from residuals. Absolute criteria give a measure of the deviation in the model outputs as compared to the observed data in the units of the observed/modelled data. Relative error criteria on the other hand give a dimensionless measure of errors in the model outputs with reference to the observed data. Relative criteria are often preferred since they can be compared across various target constituents being modelled in the dataset (Hauduc et al., 2011).

Selection of relevant goodness-of-fit criteria should take into account the modelling objectives. This research deals with the development of an exploratory model (AD-FTRW2) with the primary objective of improving pH prediction as compared to its predecessor (AD-FTRW1). This improvement on prediction accuracy of one process variable should not come at the expense of the prediction accuracy of the other measured process variables. Due to the general and comparative nature of this performance evaluation (AD-FTRW1 vs AD-FTRW2), a handful of goodness-of-fit criteria are selected out of Hauduc et al.'s (2011) classification schemes based on giving a good indication of overall and comparative model performance and are reviewed here. The selected criteria encompass measures of mean error, bias error and measures for comparsion of residuals with other models.

Two possible criteria for characterizing mean error are the Root Mean Square Error/Deviation (RMSE / RMSD) or the Mean Square Relative Error (MSRE). These criteria are very similar in that they both eliminate error compensation via their squaring operations but a difference lies in the fact that RMSE is an absolute criterion (refer to Equation 34 above) while MSRE is a relative criterion. A further difference is that MSRE emphasizes larger relative errors.

$$MSRE = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{O_i - P_i}{O_i}\right]^2$$

Equation 36: Mean Square Relative Error

Where:

n： number of data points

O_i： the observed variable at time step i

P_i： the predicted variable at time step i

Two possible criteria for quantifying bias error include Mean Error (ME) and Percent Bias (PBIAS). In both of these measures error compensation can occur and thus they do not give a good indication of the magnitude of the errors. They do however give a fair indication of systematic bias in a model whereby a model systematically over- or under-predicts. The calculation of these two criteria is outlined below (Hauduc et al., 2011). It can be seen that Mean Error is an absolute criterion and Percent Bias is a relative criterion.

$$ME = \frac{1}{n}\sum_{i=1}^{n}(O_i - P_i)$$

Equation 37: Mean Error

$$PBIAS = 100\frac{\sum_{i=1}^{n}(O_i - P_i)}{\sum_{i=1}^{n}O_i}$$

Equation 38: Percent Bias

A generalized form of a criterion for comparison of residuals with other models is suggested by Hauduc et al. (2011) as:

$$CE_{\alpha,\gamma} = 1 - \frac{\sum_{i=1}^{n}(O_i^{\alpha} - P_i^{\alpha})^{\gamma}}{\sum_{i=1}^{n}(O_i^{\alpha} - \tilde{P}_i^{\alpha})^{\gamma}}$$

Equation 39: Coefficient of Efficiency

Where:

P_i : the predicted variable at time step i and

$\widetilde{P_i}$: the predicted variable at time step i of the reference model

An example of one of these criterion is the Nash-Sutcliffe Coefficient of Efficiency where $\alpha = 1$, $\gamma = 2$ and the reference model is defined by the mean of the observed values ($\tilde{P}_i = \bar{O}$) and is referred to as the "no knowledge" model. These criteria define the improvement of using a certain model when compared to a simpler one. The measures range from $-\infty$ to 1 with negative outcomes indicating that the new model leads to worse predictions than the reference model, zero indicating no improvement in predictions from the reference model to the new model and 1 indicating that the new model describes the observed variable perfectly. A downfall of such criteria is that they do not give an indication of the difference in model complexity when comparing the two models.

2.7 Conclusion of Literature Review

The literature reveals the following scientific hypothesis:

The pH prediction in Sasol Technology's existing AD model will be improved through the incorporation of a more comprehensive ionic speciation model.

Attached to this scientific objective, the engineering objectives of this project will be the development of a detailed model describing Anaerobic Digestion of FTRW dubbed AD-FTRW2. This model will have design and control implications for these biological processes.

3 RESEARCH METHODOLOGY AND DESIGN

3.1 The Research Instrument

As the purpose of the research was to investigate whether the incorporation of a more comprehensive ionic speciation model would lead to better pH prediction than in AD-FTRW1, the research naturally adopted a mathematical modelling approach. The resultant model (AD-FTRW2) can be classified as a research model, with the significance of its development being to explore the effects of the incorporation of new physico-chemical modelling techniques into the field of AD modelling in an attempt to adequately describe anaerobic digestion dynamics. The philosophy that the modelling approach adopted was to produce the simplest (least complex) parsimonious (fewest parameters) model that would provide the best fit to experimental data (Olsson and Newell 1999). As the model was being developed out of an existing model (AD-FTRW1), the philosophy was adapted such that the fewest number of parameters should be added.

AD-FTRW2 is further based on a mechanistic and deterministic formulation where the actual/believed physics, chemistry and microbiology that govern the process together with the fundamental mass conservation laws form the theory on which the mathematical descriptions are based. The model is therefore made up of a system of differential and algebraic equations. Nutrient uptake reactions are represented differentially as dynamic mass balances while the majority of the inorganic chemistry and speciation is represented algebraically according to the assumption that these reactions reach equilibrium (Section 2.5.4). AD-FTRW2 follows the structure of its predecessors (AD-FTRW1 and UKZN's ionic speciation model), with the biological model being represented in the form of a Gujer matrix in the WEST simulation package and the ionic speciation model implemented as a C++ subroutine, and called by the WEST package at each integration step of the biological model. An example of the form of the Gujer matrix can be viewed in Figure 10.

In the development of AD-FTRW2, a similar approach to that described by Siegrist et al. (2002) was followed, i.e. the model was (i) developed based on the metabolic pathways of anaerobic digestion; (ii) checked for material balance consistency with respect to COD, C, O, H, N and charge; (iii) calibrated and finally (iv) validated on actual dynamic flow and load experimental data. This follows the classical model development approach as depicted in Figure 6. At this point, for the purposes of clarity, it is necessary to define the use of the various terms related to model development.

1) *Model Verification* refers to the process of checking the fundamental structure of a model. It is mainly concerned with verifying material balance and unit consistency.
2) *Parameter Estimation* refers to the initial assignment of values to the model parameters.
3) *Model Calibration* refers to the process of adjusting the model parameters to fit an experimental dataset.
4) *Model Validation* refers to the process of checking the performance of the model on an independent dataset (ie a dataset that was not used for calibration).
5) *Model Evauation* refers to a statistical analysis of the performance of the model relative to some experimental dataset.

In the subsequent sections of Research Methodology and Design, tasks related to the development, verification, calibration and validation of AD-FTRW2 are outlined in greater detail.

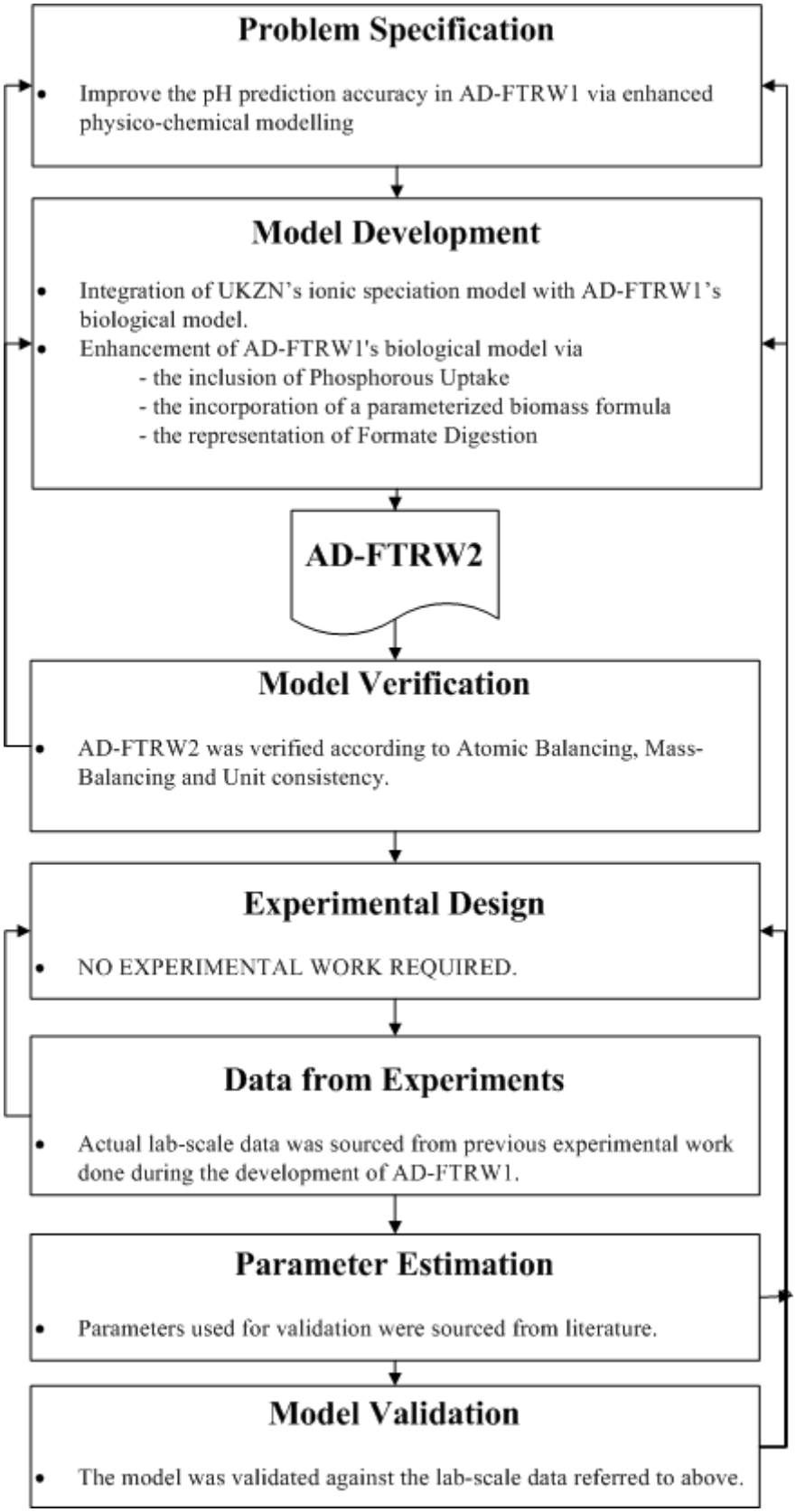

Figure 6: AD-FTRW2 model development process

Adapted from (Olsson and Newell 1999)

3.2 Hypothesis Testing

Hypothesis

The pH prediction in AD-FTRW1 will be improved through the incorporation of a more comprehensive ionic speciation model.

The testing of the abovementioned hypothesis was done via a simple comparison. On the basis of a chosen set of lab-scale data, the model predictions of AD-FTRW1 were compared with the model predictions of the modified model, dubbed AD-FTRW2, which includes the comprehensive ionic speciation. The comparative accuracies of each model were then evaluated via an F-test in order to prove or disprove the proposed hypothesis. The F-test was performed on the basis of the sum of squared residuals developed from the difference between measured and predicted variables in the data set. Below is outlined the null and alternate hypotheses from a practical and statistical perspective. (The practical perspective is an interpretation of the statistical perspective).

Null hypothesis (H_0)

Statistical perspective: The sum of squared residuals of AD-FTRW1 with respect to pH on the dataset is not significantly greater than the sum of squared residuals of AD-FTRW2.

Practical perspective: AD-FTRW2 does not provide a significantly better fit than AD-FTRW1 with respect to pH prediction.

Alternate hypothesis (H_1)

Statistical perspective: The sum of squared residuals of AD-FTRW1 with respect to pH on the dataset is significantly greater than the sum of squared residuals of AD-FTRW2.

Practical perspective: AD-FTRW2 does provide a significantly better fit than AD-FTRW1 with respect to pH prediction.

3.3 Problem Specification

The problem specification process is intended to set requirements which guide the model development process. The criteria outlined in the following sections define a benchmark for model evaluation while specifications in accuracy define a stopping point with regards to model complexity (Olsson and Newell 1999). The work involved the further development of AD-FTRW1 to form AD-FTRW2. In essence the problem was to model the anaerobic digestion of Fischer-Tropsch Reaction Water. The specifications for the model (AD-FTRW2) are outlined in the following sections.

3.3.1 *Problem*

Develop and improve Sasol Technology's existing anaerobic digestion model (AD-FTRW1) through enhanced physico-chemical modelling and with special focus on the accuracy of its pH predictions.

3.3.2 *Research Outcome*

AD-FTRW2 - A revised dynamic model of anaerobic digestion of Fischer-Tropsch reaction water that incorporates comprehensive ionic speciation modelling and that is able to accurately predict significant process variables and effluent characteristics such as reactor pH, reactor alkalinity, biogas production and effluent COD. Because (at this stage) this is a research model, no quantitative targets were imposed on the accuracy of the model.

At this stage the purpose of the model is research based, exploring the enhancement of anaerobic digestion models through the incorporation of more comprehensive physico-chemical sub-routines and through more appropriate waste stream representation. It is foreseen, however, that the work will find use for design, control and diagnosis purposes further down the line.

3.4 Model Development

Bearing the abovementioned problem specifications in mind, the following objectives for model development were identified to address the research problem:

The **primary objective** in the model development of AD-FTRW2 was to:

1) Improve the physicochemical modelling in AD-FTRW1

This would be achieved by adapting and integrating the existing biological and physico-chemical models: AD-FTRW1 and UKZN's ionic speciation model. The combining of the two models required reconciling the inorganic components represented in the biological model of AD-FTRW1 with the inorganic components represented in the speciation model. It would also be necessary to add some organic acids to the speciation model. The following developmental tasks were identified to meet the primary objective:

i) Adapt the structure of the biological model to allow it to interface with the ionic speciation model
ii) Tailor the ionic speciation model to suit FTRW (to enhance computational speed) and to allow it to interface with the biological model
iii) Enhance CO_2 expulsion/dissolution kinetics

The **secondary objective** in the model development of AD-FTRW2 is to:

2) Extend the biological modelling in AD-FTRW1

In developing the biological model two specific areas for development were identified. First of all phosphorous uptake was not previously represented in the biological processes. It was undertaken to include it in the bioprocess stioichiometry so that nutrient dosage and detailed ionic speciation of the phosphorous weak acid/base systems could be modelled. This would require the re-derivation of all bioprocesses in AD-FTRW1 so that the biomass representation ($C_kH_lO_mN_nP_p$) included phosphorous and such that this was coupled with the uptake of some sort of phosphate ion in the biological reactions. Bearing this process in mind, it was undertaken to code in a parameterized biomass formula to make the model more versatile. Further to this, a model reaction for formate digestion needed to be proposed and coded into the biological model due to the fact that it had been recognised as a significant component in FTRW. In short, the following developmental tasks were identified:

i) Included phosphorous uptake in the biological process stoichiometry via a parameterized biomass formula
ii) Model biological formate digestion

The specific tasks relating to model development that have been identified above are discussed in detail in the sections that follow. First of all an investigation into the simplifications imposed on the model via the modelling assumptions is undertaken. It was then deemed to be necessary to closely interrogate the structure of AD-FTRW1 under the philosophy that one needed to fully understand the previous work prior to attempting to improve on it. In light of this, a section is dedicated to the make-up of AD-FTRW1. Lastly, the model development section looks specifically at the biological model development and the physico-chemical model development relevant to AD-FTRW2.

3.4.1 *Modelling Assumptions*

In terms of the model development, it was important that all the model assumptions were clearly outlined as this gives an indication of where the model is or is not applicable. The following important assumptions were made and their justification follows in italics:

1) Hydrodynamics of Anaerobic Digestion is assumed to be “perfectly mixed”.

Due to relatively large Hydraulic Retention Time’s and the well-mixed mixing characteristics of the lab-scale Anaerobic Membrane Bioreactor from which experimental data was sourced for this study, it was deemed a reasonable approximation to model the Anaerobic Digester as a perfectly mixed system. This has major implications in terms of model simplification because it means that the bioreactor can be represented as a lumped parameter system without the associated complications of concentration, temperature and biomass distribution gradients

.

2) Energy Balances are not considered in the model.

Due to the sensitivity of micro-organisms to temperature fluctuations, the lab-scale Anaerobic Membrane Bioreactor from which data was sourced for this study was maintained at relatively constant temperatures and temperature was a closely monitored process variable. For Mesophilic Anaerobic Digestion this corresponds to 37°C. For this reason, there was no need to include an energy balance in the model as temperature change was negligible and this is the parameter which connects the mass and energy balances through the temperature dependence of reaction rates. Since it was so closely monitored there is not necessarily a need to model temperature as it can be measured and used as an input to the model. Temperature dependence of biological reaction rates are then taken into account by a temperature inhibition factor.

3) Liquid phase ionic speciation reactions are assumed to be at equilibrium at all integration steps.

Ultimately, an AD model consists of biological reactions which are slow (time constants of the order of days and hours) and physico-chemical reactions which are comparatively rapid (time constants of the order of minutes, seconds and milliseconds (Stumm and Morgan 1995)). This results in a system of differential equations described as stiff (due to the large range of time constants) which introduces complications in the solution of the system of equations as the size of an integration time step is limited by the time constants of the rapid reactions. In order to bypass this problem, the generally accepted approach, is to treat the physico-chemical reactions as equilibrium reactions such that they can be described as algebraic equations which greatly simplifies the solution of the system of equations. The motivation for this approach is that, from the slower reactions perspective, the faster reactions can be considered instantaneous and be assumed to always reach equilibrium before the slower reactions terminate for each time step (Rosen et al., 2005). One is then left with a system of differential and algebraic equations (DAE) which can be solved more easily than the stiff set of differential equations (Batstone et al., 2002).

3.4.2 *AD-FTRW1*

To fulfil objectives, all 21 bioprocesses represented in AD-FTRW1 had to be rederived for inclusion in AD-FTRW2. The procedure for all processes was similar; the derivation for a representative process, acetoclastic methanogenesis is presented in detail here.

The result of adapting the generalized anaerobic digestion bioprocess formulation (Ekama 2009) to acetoclastic methanogenesis was treated as the starting point.

$$\frac{5}{2Y_{am}} C_2H_4O_2 + NH_4^+ + HCO_3^- \rightarrow 4H_2O + \left(\frac{5-3Y_{am}}{2Y_{am}}\right) CO_2 + C_5H_7O_2N + \left(\frac{5-5Y_{am}}{2Y_{am}}\right) CH_4$$

Equation 40: Acetoclastic Methanogenesis

According to model assumption 2 (from section 2.5.3a.i), all CO_2 produced was re-expressed in its soluble form (H_2CO_3) by combining it with some of the H_2O produced. The speciation of the influent SCFAs was accounted

for by incorporating a parameter (F) into the bioprocess stoichiometry that described the degree of dissociation of each SCFA. In terms of F, Acetic acid speciates according to the following relationship:

$$\boldsymbol{C_2H_4O_2 \rightarrow (1-F)C_2H_4O_2 + FC_2H_3O_2^- + FH^+}$$

Equation 41: Acetic acid dissociation

By representing CO_2 in its soluble form and substituting Equation 41 into Equation 40 with HCO_3^- treated as the proton sink, some simple algebraic manipulations yielded the final model equation for acetoclastic methanogenesis in AD-FTRW1.

$$\frac{\mathbf{5(1-F)}}{\mathbf{2Y_{am}}}\boldsymbol{C_2H_4O_2} + \frac{\mathbf{5F}}{\mathbf{2Y_{am}}}\boldsymbol{C_2H_3O_2^-} + \boldsymbol{NH_4^+} + \frac{\mathbf{(5-11Y_{am})}}{\mathbf{2Y_{am}}}\boldsymbol{H_2O} + \frac{\mathbf{(5F+3Y_{am}-5)}}{\mathbf{2Y_{am}}}\boldsymbol{H_2CO_3} \rightarrow \frac{\mathbf{(5F-2Y_{am})}}{\mathbf{2Y_{am}}}\boldsymbol{HCO_3^-} + \boldsymbol{C_5H_7O_2N} + \frac{\mathbf{(5-5Y_{am})}}{\mathbf{2Y_{am}}}\boldsymbol{CH_4}$$

Equation 42: AD-FTRW1's Acetoclastic Methanogenesis

A full representation of AD-FTRW1 in its Gujer matrix form is presented in the appendix.

It is interesting to note how the interaction of the organic processes with the inorganic chemistry was previously implemented in AD-FTRW1. The defining assumptions relating to the previous modelling approach are summarized below:

- All CO_2 produced biologically is represented in its soluble form (H_2CO_3).
- The carbonate system acts as the proton source/sink for all weak acid base chemistry reactions.
- The contribution of CO_3^{2-} is regarded as negligible in the anaerobic digestion pH range.
- Only the protonated (non-ionic) form of any SCFA can be metabolized.
- An un-protonated (ionic) SCFA must first pick up a proton from the carbonate system prior to its metabolism:
- The degree to which influent SCFA's dissociate is determined by the influent pH.
- Biomass is represented in the bioprocess stoichiometry as $C_5H_7O_2N$

In summary, AD-FTRW1 uses a simplification of the approach developed by Musvoto et al. (2000) in order to represent ionic speciation. An approximate representation of the dominant weak acid-base systems (the carbonate, ammonia and organic acid systems), was derived for a limited pH range (6.5 – 7.5) and embedded into the stoichiometry of the biological reactions. The assumption that the pH will remain in this range is the major limitation of AD-FTRW1.

3.4.3 *AD-FTRW2*

In the revised model (AD-FTRW2), all assumptions with regards to the inorganic carbon weak acid base system were dropped and all SCFA speciation that was previously integrated into the stoichiometry was removed. This

meant that the organic process stoichiometry which would be implemented in the newly coded Gujer matrix would be similar to Equation 40; a direct result of the derivation techniques outlined byEkama (2009).

The new approach is to make no assumptions as to the speciation of any relevant species, but rather to actually calculate the ionic speciation via a "C " script that is coded with the relevant equilibrium chemistry and that communicates with the WEST solver at each integration step in order to improve the accuracy of the organic – inorganic interactions represented in the model.

In short, to extend the pH range that can be modeled, AD-FTRW2 uses an ionic speciation sub-model which considers all the relevant acid/base subsystems, and is capable of predicting pH over the range 3.5 to 9 (assuming that the relevant chemical analyses are available and accurate).

In the sections that follow, the model development tasks associated with the construction of AD-FTRW2 are described in detail. The description is divided into those tasks related to biological model development and then those tasks related to physico-chemical model development although oftentimes this distinction was not so clear when performing work necessary to interface the biological model with the ionic speciation sub-routine.

a. ***Biological model development***

i. **Total Components**

A set of total components was selected and implemented on the biological side of the model in order to make the WEST model compatible with the ionic speciation sub-routine. A single component that was representative of each significant ionic system had to be selected and included as a WEST model component. This component would represent the total concentration of all of the sub-species relevant to that ionic system. This task is theoretically related to the physico-chemical model development but since it involved significant changes to the biological model structure, it has been included as part of the work done in Biological model development. The set of components selected for use in programming the Gujer Matrix in WEST are depicted in the table on the following page.

Table 7: Biological Model Components

No:	*Component*	*Formula*	*No:*	*Component*	*Formula*
1	Water	H_2O		*Particulates*	
	Solubles		*18*	S_{bp}	$CH_lO_mN_nP_p$
2	Hydrogen	H_2	*19*	Z_{ad}	$CH_lO_mN_nP_p$
3	Proton	H^+	*20*	Z_{acHx}	$CH_lO_mN_nP_p$
4	Carbonate	CO_3^{2-}	*21*	Z_{acVa}	$CH_lO_mN_nP_p$
5	Ammonium	NH_4^+	*22*	Z_{acBu}	$CH_lO_mN_nP_p$
6	Phosphate	PO_4^{3-}	*23*	Z_{acPr}	$CH_lO_mN_nP_p$
7	Hexanoate	$C_6H_{11}O_2^-$	*24*	Z_{acEt}	$CH_lO_mN_nP_p$
8	Valerate	$C_5H_9O_2^-$	*25*	Z_{am}	$CH_lO_mN_nP_p$
9	Butyrate	$C_4H_7O_2^-$	*26*	Z_{mm}	$CH_lO_mN_nP_p$
10	Propionate	$C_3H_5O_2^-$	*27*	Z_{hm}	$CH_lO_mN_nP_p$
11	Acetate	$C_2H_3O_2^-$	*28*	Z_{fd}	$CH_lO_mN_nP_p$
12	Formate	CHO_2^-	*29*	Z_e	$CH_lO_mN_nP_p$
13	Sodium ion	Na^+		*Gases*	
14	Chloride	Cl^-	*30*	Carbon Dioxide	CO_2
15	Ethanol	C_2H_6O	*31*	Methane	CH_4
16	Methanol	CH_4O			
17	Urea	$(NH_2)_2CO$			

It is important to note that components have been included to allow for the representation of phosphorous uptake by the biomass; phosphate and $CH_lO_mN_nP_p$. For values of $p \neq 0$ in the parameterized biomass formula, the biomass model component depicts the uptake of phosphorous during the bioprocesses in which it is involved. This was not possible in AD-FTRW1 where phosphorous uptake was ignored. The inclusion of the parameterized biomass formula also helps to make the model more versatile in that, should the biomass of different systems exhibit a significantly different make-up in terms of its C, H, O, N and P constitution, the model can be easily adapted via these parameters. This means that the stoichiometry of the bioprocesses is also linked to these parameters.

ii. Selection of basis for stoichiometry formulation: substrate consumption vs. biomass production

During the development of the model, another complication was erroneously encountered in the development of the bioprocess stoichiometry. It is discussed here to highlight the effect of such an error and to highlight the fact that care must be taken in biological systems to avoid such mistakes. In the first iteration of biological process stoichiometry derivation the basis for the derivation was inconsistently defined. In all the processes the stoichiometry was derived in terms of 1 mole of substrate being consumed instead of in terms of 1 mole of biomass being produced (which was the convention used in AD-FTRW1). While this does not have any bearing

on the ratios in which reactants and products are consumed and produced in a reaction, this does have implications on the rates at which various components are assimilated and the comparative speeds of the various processes. The convention to use depends on the formulation of the rate expressions and since the rate expressions were sourced from AD-FTRW1 the same fundamental convention had to be adopted. To re-express all bioprocesses in AD-FTRW2 in terms of 1 mole of biomass being produced was identified to be a time-consuming process. Instead the rate expressions in AD-FTRW2 were scaled by the reciprocal of the stoichiometric co-efficient for the FOG in each bioprocess (refer to Table 8 in Bioprocess Kinetics). This meant that although the stoichiometry still appears in the Gujer Matrix in terms of 1 mole of substrate being utilized, the rate expressions were scaled such that the net effect on the differential equations was equivalent to AD-FTRW1. This is because the rate of consumption or generation of a component in a process is given by the product of that component's stoichiometric co-efficient and the rate expression. It is important to use a consistent approach across bioprocesses and models such that rate parameters are comparable intra-model and inter-model. The representation of bioprocess stoichiometry on the basis of 1 mole of biomass being produced is recognized as a significant part of the model development process.

iii. Bioprocesses Stoichiometry

Sotemann et al. (2006) presented a generalised formulation for the stoichiometry of anaerobic processes. This formulation was adopted to derive all of the bioprocess stoichiometry in AD-FTRW2. As before, the procedure will be illustrated using acetoclastic methanogenesis as an example.

As with all the biologically mediated transformations, acetoclastic methanogenesis consists of an *anabolic* part, which describes the growth of biomass on a substrate, and a *catabolic* part, which provides the energy for the process. Adapted to the components used in this model, the generalized expression for the anabolic reaction becomes:

$$\begin{aligned} C_xH_yO_zN_aP_b \rightarrow\ & C_kH_lO_mN_nP_p + \left(3b+2x-a+\left(n-3p-2k\right)\cdot\frac{\gamma_S}{\gamma_B}\right)H^+ \\ & + \left(z-3x-4b+\left(3k-m+4p\right)\cdot\frac{\gamma_S}{\gamma_B}\right)H_2O + \left(x-k\cdot\frac{\gamma_S}{\gamma_B}\right)CO_3^{=} \\ & + \left(a-n\cdot\frac{\gamma_S}{\gamma_B}\right)NH_4^+ + \left(b-p\cdot\frac{\gamma_S}{\gamma_B}\right)PO_4^{-3} \end{aligned}$$

Equation 43: Generalized biological anabolic reaction

where $\gamma_S = 4x+y-2z-3a+5b$ and $\gamma_B = 4k+l-2m-3n+5p$ are the redox electrons per mole for the two organic components and are usually referred to as the electron donating capacity of the substrate and the electron accepting capacity of the biomass respectively.

For acetoclastic methanogenesis, the substrate $C_xH_yO_zN_aP_b$ is acetic acid, so x=2, y=4, z=2 and a=b=0. Also acetic acid is represented in the model component scheme as H^+ + Ac^-. The product $C_kH_lO_mN_nP_p$ is biomass.

The accompanying catabolic reaction is $CH_3COOH \rightarrow CO_2 + CH_4$ which, in terms of the model components becomes:

$$H^+ + Ac^- + H_2O \rightarrow 2H^+ + CO_3^{=} + CH_4$$

Equation 44: Acetoclastic methanogenesis catabolic reaction

Finally, the reactions are linked in the combination $Y_{AM} \cdot \text{anabolic} + (1 - Y_{AM}) \cdot \text{catabolic}$, where Y_{AM} is the yield coefficient for acetoclastic methanogens. Collecting the terms for each component provides the resultant bioprocess stoichiometry and the coefficient expressions to be entered into the Gujer matrix of the model (Equation 46). The same general procedure was applied to all the biological reactions.

In order to make the process of coding in WEST faster and less prone to human error, generalized expressions for the relevant bioprocesses (acetogenesis and methanogenesis) were derived and coded into Matlab in order to exploit the software's "symbolic maths" capabilities. This meant that the code could be run by simply entering in substrate and biomass parameters and it would automatically generate the correct stoichiometric coefficients for the components relevant to that bioprocess. For the purposes of maintaining a parameterized biomass formula for increased model versatility, only the substrate parameters ($C_xH_yO_zN_aP_b$) were specified in the execution of the code. Since there was only one process relevant to hydrolysis and acidogenesis it was not necessary to formulate a generalized equation for this bioprocess. The derivation for these generalized expressions can be found in the appendix along with the associated Matlab codes. (Refer to sections 7.2, 7.3 and 7.4 in appendix).

Using the aforementioned generalized expressions for the relevant bioprocesses in the context of the matlab bioprocess stoichiometry generators, the biological side of the model was coded in WEST via the Gujer Matrix platform in the Model Editor.

The stoichiometry generators were designed using components that were compatible with the ionic speciation sub-routine that was to be integrated with the biological model as was discussed in section 3.4.3a.i above. The stoichiometry for every bioprocess that was represented in AD-FTRW1 was regenerated and recoded for AD-FTRW2. Below is a comparison of the structure of the bioprocesses in AD-FTRW1&2. Equation 45 and Equation 46 give the representations of the acetoclastic methanogenesis process in the two models and help to highlight the structural changes that were necessary in order to integrate the biological model in AD-FTRW2 with the ionic speciation sub-routine.

$$\frac{5(1-F)}{2Y_{am}}C_2H_4O_2 + \frac{5F}{2Y_{am}}C_2H_3O_2^- + NH_4^+ + \frac{(5-11Y_{am})}{2Y_{am}}H_2O + \frac{(5F+3Y_{am}-5)}{2Y_{am}}H_2CO_3 \rightarrow \frac{(5F-2Y_{am})}{2Y_{am}}HCO_3^- + C_5H_7O_2N + \frac{(5-5Y_{am})}{2Y_{am}}CH_4$$

Equation 45: Acetoclastic Methanogenesis AD-FTRW1

$$C_2H_3O_2^- + \frac{8Y_{am}n}{\gamma_B}NH_4^+ + \left(3Y_{am} - \frac{8Y_{am}(4p-m+3)}{\gamma_B} + 1\right)H_2O + \frac{8Y_{am}p}{\gamma_B}PO_4^{3-} \rightarrow \left(Y_{am} - \frac{8Y_{am}}{\gamma_B} + 1\right)CO_3^{2-} + \left(2Y_{am} - \frac{8Y_{am}(3p-n+2)}{\gamma_B} + 1\right)H^+ + \frac{8Y_{am}}{\gamma_B}C_1H_lO_mN_nP_p + (1-Y_{am})CH_4$$

Equation 46: Acetoclastic Methanogenesis AD-FTRW2

1) In Equation 45, the chemical entities NH_4^+, HCO_3^- and H_2CO_3, represent free ionic species.
2) In Equation 46, all chemical entities representing dissolved species ($C_2H_3O_2^-$, NH_4^+, $CO_3^=$, PO_4^{-3}, H^+) no longer represent the ionic species, but rather total dissolved concentrations (i.e. total acetate, total ammonia, total carbonate, total phosphate etc.). These total dissolved concentrations are inputs to the speciation sub-model, which calculates the free species concentrations in the underlying sub-systems.

A full representation of the biological model of AD-FTRW2 is depicted in the Gujer matrix presented in the results section. Below is a list of all remaining bioprocess stoichiometric equations in AD-FTRW2. In terms of the reaction stoichiometry, all components are expressed on the right hand side of the reaction equation. This means that all reactants have negative co-efficients and all products have positive co-efficients. Furthermore the bioprocess stoichiometry was developed on the basis of 1 mole of substrate being utilized in each reaction so as to standardize the approach and make reaction kinetic constants more comparable. Superscripts to the biomass components in the equations below of the form Z_{xx} show the abbreviated symbols used for those biomass FOGs. In Equation 47 for instance Z_{ad} is the symbol for the biomass responsible for acidogenesis. Abbreviations such as ad, achx etc are explained in the List of Acronyms/Abbreviations at the beginning of this thesis but assume logical abbreviations of the biological process in which they are involved.

$$\mathbf{0} \rightarrow (Y_{ad})\boldsymbol{CH_lO_mN_nP_p^{Zad}} + (-1)\boldsymbol{CH_lO_mN_nP_p^{Sbp}} + \left(\frac{-Gb(Y_{ad}-1)}{8}\right)\boldsymbol{C_2H_3O_2^-} + \frac{Gb\left(\frac{32p-8m+24}{Gb}-4\right)(Y_{ad}-1)}{8}\boldsymbol{H_2O} + \frac{-Gb\left(\frac{24p-8n+16}{Gb}-3\right)(Y_{ad}-1)}{8}\boldsymbol{H^+} + \frac{-Gb\left(\frac{8}{Gb}-2\right)(Y_{ad}-1)}{8}\boldsymbol{CO_3^{2-}} + \left(-n(Y_{ad}-1)\right)\boldsymbol{NH_4^+} + \left(-p(Y_{ad}-1)\right)\boldsymbol{PO_4^{3-}}$$

Equation 47: Acidogenesis

$$\mathbf{0} \rightarrow \left(\frac{32Y_{acHx}}{\gamma_b}\right)\boldsymbol{CH_lO_mN_nP_p^{Z_{acHx}}} + (-1)\boldsymbol{C_6H_{11}O_2^-} + (1-Y_{acHx})\boldsymbol{C_4H_7O_2^-} + (1-Y_{acHx})\boldsymbol{C_2H_3O_2^-}$$
$$+ \left(2Y_{acHx} + Y_{acHx}\left(\frac{128p-32m+96}{\gamma_b} - 16\right) - 2\right)\boldsymbol{H_2O}$$
$$+ \left(-Y_{acHx} - Y_{acHx}\left(\frac{96p-32n+64}{\gamma_b} - 11\right) + 1\right)\boldsymbol{H^+} + \left(-Y_{acHx}\left(\frac{32}{\gamma_b} - 6\right)\right)\boldsymbol{CO_3^{2-}}$$
$$+ \left(\frac{-32Y_{acHx}n}{\gamma_b}\right)\boldsymbol{NH_4^+} + \left(\frac{-32Y_{acHx}p}{\gamma_b}\right)\boldsymbol{PO_4^{3-}} - \left(2(Y_{acHx}-1)\right)\boldsymbol{H_2}$$

Equation 48: Hexanoic Acid Acetogenesis

$$\mathbf{0} \rightarrow \left(\frac{26Y_{acVa}}{\gamma_b}\right)\boldsymbol{CH_lO_mN_nP_p^{Z_{acVa}}} + (-1)\boldsymbol{C_5H_9O_2^-} + (1-Y_{acVa})\boldsymbol{C_3H_5O_2^-} + (1-Y_{acVa})\boldsymbol{C_2H_3O_2^-}$$
$$+ \left(2Y_{acVa} + Y_{acVa}\left(\frac{104p-26m+78}{\gamma_b} - 13\right) - 2\right)\boldsymbol{H_2O}$$
$$+ \left(-Y_{acVa} - Y_{acVa}\left(\frac{78p-26n+52}{\gamma_b} - 9\right) + 1\right)\boldsymbol{H^+} + \left(-Y_{acVa}\left(\frac{26}{\gamma_b} - 5\right)\right)\boldsymbol{CO_3^{2-}}$$
$$+ \left(\frac{-26Y_{acVa}n}{\gamma_b}\right)\boldsymbol{NH_4^+} + \left(\frac{-26Y_{acVa}p}{\gamma_b}\right)\boldsymbol{PO_4^{3-}} - \left(2(Y_{acVa}-1)\right)\boldsymbol{H_2}$$

Equation 49: Valeric Acid Acetogenesis

$$\mathbf{0} \rightarrow \left(\frac{20Y_{acBu}}{\gamma_b}\right)\boldsymbol{CH_lO_mN_nP_p^{Z_{acBu}}} + (-1)\boldsymbol{C_4H_7O_2^-} + \left(2(1-Y_{acBu})\right)\boldsymbol{C_2H_3O_2^-}$$
$$+ \left(2Y_{acBu} + Y_{acBu}\left(\frac{80p-20m+60}{\gamma_b} - 10\right) - 2\right)\boldsymbol{H_2O}$$
$$+ \left(-Y_{acBu} - Y_{acBu}\left(\frac{60p-20n+40}{\gamma_b} - 7\right) + 1\right)\boldsymbol{H^+} + \left(-Y_{acBu}\left(\frac{20}{\gamma_b} - 4\right)\right)\boldsymbol{CO_3^{2-}}$$
$$+ \left(\frac{-20Y_{acBu}n}{\gamma_b}\right)\boldsymbol{NH_4^+} + \left(\frac{-20Y_{acBu}p}{\gamma_b}\right)\boldsymbol{PO_4^{3-}} - \left(2(Y_{acBu}-1)\right)\boldsymbol{H_2}$$

Equation 50: Butyric Acid Acetogenesis

$$\mathbf{0} \rightarrow \left(\frac{14Y_{acPr}}{\gamma_b}\right)\boldsymbol{CH_lO_mN_nP_p^{Z_{acPr}}} + (-1)\boldsymbol{C_3H_5O_2^-} + (1-Y_{acPr})\boldsymbol{C_2H_3O_2^-}$$
$$+ \left(3Y_{acPr} + Y_{acPr}\left(\frac{56p-14m+42}{\gamma_b} - 7\right) - 3\right)\boldsymbol{H_2O}$$
$$+ \left(-2Y_{acPr} - Y_{acPr}\left(\frac{42p-14n+28}{\gamma_b} - 5\right) + 2\right)\boldsymbol{H^+}$$
$$+ \left(1 - Y_{acBu}\left(\frac{14}{\gamma_b} - 3\right) - Y_{acBu}\right)\boldsymbol{CO_3^{2-}} + \left(\frac{-14Y_{acBu}n}{\gamma_b}\right)\boldsymbol{NH_4^+} + \left(\frac{-14Y_{acBu}p}{\gamma_b}\right)\boldsymbol{PO_4^{3-}}$$
$$- \left(3(Y_{acBu}-1)\right)\boldsymbol{H_2}$$

Equation 51: Propionic Acid Acetogenesis

$$\mathbf{0} \rightarrow \left(\frac{12Y_{acEt}}{\gamma_b}\right)\boldsymbol{CH_lO_mN_nP_p^{Z_{acEt}}} + (-1)\boldsymbol{C_2H_6O} + (1 - Y_{acEt})\boldsymbol{C_2H_3O_2^-} + \left(Y_{acEt} + Y_{acEt}\left(\frac{48p - 12m + 36}{\gamma_b} - 5\right) - 1\right)\boldsymbol{H_2O} + \left(-Y_{acEt} - Y_{acEt}\left(\frac{36p - 12n + 24}{\gamma_b} - 4\right) + 1\right)\boldsymbol{H^+} + \left(-Y_{acEt}\left(\frac{12}{\gamma_b} - 2\right)\right)\boldsymbol{CO_3^{2-}} + \left(\frac{-12Y_{acEt}n}{\gamma_b}\right)\boldsymbol{NH_4^+} + \left(\frac{-12Y_{acEt}p}{\gamma_b}\right)\boldsymbol{PO_4^{3-}} - \left(2(Y_{acEt} - 1)\right)\boldsymbol{H_2}$$

Equation 52: Ethanol Acetogenesis

$$\mathbf{0} \rightarrow \left(\frac{6Y_{mm}}{\gamma_b}\right)\boldsymbol{CH_lO_mN_nP_p^{Z_{mm}}} + (-1)\boldsymbol{CH_4O} + \left(Y_{mm}\left(\frac{24p - 6m + 18}{\gamma_b} - 2\right) - \frac{Y_{mm}}{4} + \frac{1}{4}\right)\boldsymbol{H_2O} + \left(\frac{1}{2} - Y_{mm}\left(\frac{18p - 6n + 12}{\gamma_b} - 2\right) - \frac{Y_{mm}}{2}\right)\boldsymbol{H^+} + \left(\frac{1}{4} - Y_{mm}\left(\frac{6}{\gamma_b} - 1\right) - \frac{Y_{mm}}{4}\right)\boldsymbol{CO_3^{2-}} + \left(\frac{-6Y_{mm}n}{\gamma_b}\right)\boldsymbol{NH_4^+} + \left(\frac{-6Y_{mm}p}{\gamma_b}\right)\boldsymbol{PO_4^{3-}} + \left(\frac{3}{4} - \frac{3Y_{mm}}{4}\right)\boldsymbol{CH_4}$$

Equation 53: Methanol Methanogenesis

$$\mathbf{0} \rightarrow \left(\frac{8Y_{am}}{\gamma_b}\right)\boldsymbol{CH_lO_mN_nP_p^{Z_{am}}} + (-1)\boldsymbol{C_2H_3O_2^-} + \left(-3Y_{am} + \left(\frac{8Y_{am}(4p - m + 3)}{\gamma_b}\right) - 1\right)\boldsymbol{H_2O} + \left(2Y_{am} - \left(\frac{8Y_{am}(3p - n + 2)}{\gamma_b}\right) + 1\right)\boldsymbol{H^+} + \left(Y_{am} - \frac{8Y_{am}}{\gamma_b} + 1\right)\boldsymbol{CO_3^{2-}} + \left(\frac{-8Y_{am}n}{\gamma_b}\right)\boldsymbol{NH_4^+} + \left(\frac{-8Y_{am}p}{\gamma_b}\right)\boldsymbol{PO_4^{3-}} + (1 - Y_{am})\boldsymbol{CH_4}$$

Equation 54: Acetoclastic Methanogenesis

$$\mathbf{0} \rightarrow \left(\frac{2Y_{hm}}{\gamma_b}\right)\boldsymbol{CH_lO_mN_nP_p^{Z_{hm}}} + (\mathbf{-1})\boldsymbol{H_2} + \left(\left(\frac{Y_{hm}(8p - 2m + 6)}{\gamma_b}\right) - \frac{3Y_{hm}}{4} + \frac{3}{4}\right)\boldsymbol{H_2O} + \left(\frac{Y_{hm}}{2} - \left(\frac{Y_{hm}(6p - 2n + 4)}{\gamma_b}\right) - \frac{1}{2}\right)\boldsymbol{H^+} + \left(\frac{Y_{hm}}{4} - \frac{2Y_{hm}}{\gamma_b} - \frac{1}{4}\right)\boldsymbol{CO_3^{2-}} + \left(\frac{-2Y_{hm}n}{\gamma_b}\right)\boldsymbol{NH_4^+} + \left(\frac{-2Y_{hm}p}{\gamma_b}\right)\boldsymbol{PO_4^{3-}} + \left(\frac{1}{4} - \frac{Y_{hm}}{4}\right)\boldsymbol{CH_4}$$

Equation 55: Hydrogenotrophic Methanogenesis

$$\mathbf{0} \rightarrow -\boldsymbol{(NH_2)_2CO} - \boldsymbol{2H_2O} + \boldsymbol{CO_3^{2-}} + \boldsymbol{2NH_4^+}$$

Equation 56: Urea Hydrolysis

$$\mathbf{0} \rightarrow \left(\frac{2Y_{fd}}{\gamma_b}\right)\boldsymbol{CH_lO_mN_nP_p^{Z_{fd}}} + (-1)\boldsymbol{CHO_2^-} + \left(Y_{fd} + Y_{fd}\left(\frac{8p - 2m + 6}{\gamma_b} - 1\right) - 1\right)\boldsymbol{H_2O} + \left(-Y_{fd} - Y_{fd}\left(\frac{6p - 2n + 4}{\gamma_b} - 1\right) + 1\right)\boldsymbol{H^+} + \left(1 - Y_{fd}\left(\frac{2}{\gamma_b} - 1\right) - Y_{fd}\right)\boldsymbol{CO_3^{2-}} + \left(\frac{-2Y_{fd}n}{\gamma_b}\right)\boldsymbol{NH_4^+} + \left(\frac{-2Y_{fd}p}{\gamma_b}\right)\boldsymbol{PO_4^{3-}} + \left(1 - Y_{fd}\right)\boldsymbol{H_2}$$

Equation 57: Formate Digestion

$$CH_lO_mN_nP_p^{Z_{xx}} \rightarrow (1-f)CH_lO_mN_nP_p^{S_{bp}} + fCH_lO_mN_nP_p^{Z_e}$$

Equation 58: Biomass Death

Where the "xx" subscript is adopted to denote the biomass of each FOG separately and so can take on the following labels explained in the List of Acronyms/Abbreviations: ad, acHx, acVa, acBu, acPr, acEt, mm, am and hm.

iv. Bioprocess Kinetics

The rate expressions for the various bioprocesses in AD-FTRW2 were sourced from AD-FTRW1. A difference exists in the fact that the rate expressions have been scaled by the reciprocal of the stoichiometric co-efficient to the FOG for that process. This difference is explained later on in the discussion (section 0). The kinetics as they were applied are depicted in Table 8. All parameters take on the same values that were presented in the literature review of AD-FTRW1. It must also be noted that only growth kinetics are depicted in the table. All death kinetics are first order with respect to that FOG and due to their simplicity they are not depicted below.

Table 8: AD-FTRW2 Bioprocess Kinetics

Processes		*Process Rates*
1	***ad***	$\left(\frac{1}{Y_{ad}}\right)\frac{\mu_{max\,Ad}\,S_{bp}}{(K_{sAd}+S_{bp})}Z_{Ad}\left(\frac{1+10^{-0.5(T_{LL}-T_{UL})}}{1+10^{(T_r-T_{UL})}+10^{(T_{LL}-T_r)}}\right)\left(\frac{1+10^{-0.43(pH_{LLZadZac}-pH_{ULZadZac})}}{1+10^{(pH_r-pH_{ULZadZac})}+10^{(pH_{LLZadZac}-pH_r)}}\right)\left(1-\frac{[H_{2(aq)}]}{k_{l.H_2Z_{ad}}+[H_{2(aq)}]}\right)$
3	***acHx***	$\left(\frac{\gamma_B}{32Y_{acHx}}\right)\frac{\mu_{max\,acHx}\,Hx}{(K_{sacHx}+Hx)}Z_{acHx}\left(\frac{1+10^{-0.5(T_{LL}-T_{UL})}}{1+10^{(T_r-T_{UL})}+10^{(T_{LL}-T_r)}}\right)\left(\frac{1+10^{-0.43(pH_{LLZadZac}-pH_{ULZadZac})}}{1+10^{(pH_r-pH_{ULZadZac})}+10^{(pH_{LLZadZac}-pH_r)}}\right)\left(\frac{1}{1+\frac{H_2}{k_{H_2Zac}}}\right)$
5	***acVa***	$\left(\frac{\gamma_B}{26Y_{acVa}}\right)\frac{\mu_{max\,acVa}\,Va}{(K_{sacVa}+Va)}Z_{acVa}\left(\frac{1+10^{-0.5(T_{LL}-T_{UL})}}{1+10^{(T_r-T_{UL})}+10^{(T_{LL}-T_r)}}\right)\left(\frac{1+10^{-0.43(pH_{LLZadZac}-pH_{ULZadZac})}}{1+10^{(pH_r-pH_{ULZadZac})}+10^{(pH_{LLZadZac}-pH_r)}}\right)\left(\frac{1}{1+\frac{H_2}{k_{H_2Zac}}}\right)$
7	***acBu***	$\left(\frac{\gamma_B}{20Y_{acBu}}\right)\frac{\mu_{max\,acBu}\,Bu}{(K_{sacBu}+Bu)}Z_{acBu}\left(\frac{1+10^{-0.5(T_{LL}-T_{UL})}}{1+10^{(T_r-T_{UL})}+10^{(T_{LL}-T_r)}}\right)\left(\frac{1+10^{-0.43(pH_{LLZadZac}-pH_{ULZadZac})}}{1+10^{(pH_r-pH_{ULZadZac})}+10^{(pH_{LLZadZac}-pH_r)}}\right)\left(\frac{1}{1+\frac{H_2}{k_{H_2Zac}}}\right)$
9	***acPr***	$\left(\frac{\gamma_B}{14Y_{acPr}}\right)\frac{\mu_{max\,acPr}\,Pr}{(K_{sacPr}+Pr)}Z_{acPr}\left(\frac{1+10^{-0.5(T_{LL}-T_{UL})}}{1+10^{(T_r-T_{UL})}+10^{(T_{LL}-T_r)}}\right)\left(\frac{1+10^{-0.43(pH_{LLZadZac}-pH_{ULZadZac})}}{1+10^{(pH_r-pH_{ULZadZac})}+10^{(pH_{LLZadZac}-pH_r)}}\right)\left(\frac{1}{1+\frac{H_2}{k_{H_2Zac}}}\right)\left(\frac{1}{1+\frac{SCFA}{k_{SCFAZac}}}\right)$
11	***acEt***	$\left(\frac{\gamma_B}{12Y_{acEt}}\right)\frac{\mu_{max\,acEt}\,Et}{(K_{sacEt}+Et)}Z_{acEt}\left(\frac{1+10^{-0.5(T_{LL}-T_{UL})}}{1+10^{(T_r-T_{UL})}+10^{(T_{LL}-T_r)}}\right)\left(\frac{1+10^{-0.43(pH_{LLZadZac}-pH_{ULZadZac})}}{1+10^{(pH_r-pH_{ULZadZac})}+10^{(pH_{LLZadZac}-pH_r)}}\right)\left(\frac{1}{1+\frac{H_2}{k_{H_2Zac}}}\right)$
13	***mm***	$\left(\frac{\gamma_B}{6Y_{mm}}\right)\frac{\mu_{max\,MM}\,Me}{(K_{sMM}+Me)}Z_{MM}\left(\frac{1+10^{-0.5(T_{LL}-T_{UL})}}{1+10^{(T_r-T_{UL})}+10^{(T_{LL}-T_r)}}\right)\left(\frac{1+10^{-0.43(pH_{LLZmmZhm}-pH_{ULZmmZhm})}}{1+10^{(pH_r-pH_{ULZmmZhm})}+10^{(pH_{LLZmmZhm}-pH_r)}}\right)$
15	***am***	$\left(\frac{\gamma_B}{8Y_{am}}\right)\frac{\mu_{max\,MM}\,Me}{(K_{sMM}+Me)}Z_{MM}\left(\frac{1+10^{-0.5(T_{LL}-T_{UL})}}{1+10^{(T_r-T_{UL})}+10^{(T_{LL}-T_r)}}\right)\left(\frac{1+10^{-0.43(pH_{LLZmmZhm}-pH_{ULZmmZhm})}}{1+10^{(pH_r-pH_{ULZmmZhm})}+10^{(pH_{LLZmmZhm}-pH_r)}}\right)$
17	***hm***	$\left(\frac{\gamma_B}{2Y_{hm}}\right)\frac{\mu_{\max\,j}S_j}{(K_{sj}+S_j)}Z_{Aj}\left(\frac{1+10^{-0.5(T_{LL}-T_{UL})}}{1+10^{(T_r-T_{UL})}+10^{(T_{LL}-T_r)}}\right)\left(\frac{1+10^{pHj(pH_{LLZj}-pH_{ULZj})}}{1+10^{(pH_r-pH_{ULZj})}+10^{(pH_{LLZj}-pH_r)}}\right)\left(1-\frac{[H_{2(aq)}]}{k_{l.H_2Z_{ad}}+[H_{2(aq)}]}\right)$

v. Final differential equations

AD-FTRW2 was developed on the WEST modelling software. In this modelling software system reactions are conveniently programmed in the Gujer matrix interface of the model editor environment. As was mentioned in the literature review, the Gujer matrix is a structured representation of reactions (presented in each row), components (presented in each column) and reaction rates (presented in the final column) that are involved in a reactor model (Vanhooren et al., 2003). The body of the Gujer matrix contains the stoichiometric coefficents of the components in the various reactions and the rates of each reaction in the final column. WEST then has an automated code generator which uses this structured representation (Gujer matrix) to generate the set of differential equations governing the system. Since all differential equations have a similar form it is considered repetitive and unnecessary to present the entire set of differential equations. Instead a generalized structure of the differential equations is presented here.

$$\frac{dM_i}{dt} = F_i^{in} - F_i^{out} + V_{reactor} \sum_{r=1}^{j} \mathrm{v}_i^r \times r^r$$

Equation 59: Generalized structure of differential equations in AD-FTRW2

Where:

M_i is the mass of component i in the reactor

F_i is the mass flow of component i into or out of the reactor

$V_{reactor}$ is the volume of the reactor

v_i^r is the stoichiometric coefficient of component i in reaction r

And r^r is the specific reaction rate of reaction r on the basis of reactor volume and in terms of mass

b. *Physico-chemical model development*

i. Ionic Speciation

In order to reduce computational time whilst maintaining a good level of accuracy in the model, it was decided to come up with a criterion for the inclusion of ionic species, based on a Fischer-Tropsch Reaction Water Analysis. The information on which the results are based is the Synthetic Fischer-Tropsch Reaction Water recipe (van Zyl 2008) which can be found in the appendix (refer to section **Error! Reference source not ound.**).

An inorganic component analysis was inputted into MinteqA2 in order to retrieve the equilibrated mass distribution of the inorganic species in the wastewater. Following the MinteqA2 analysis, conclusions could be made as to which inorganic systems and sub-species to include in the ionic speciation model tailored for Fischer-Tropsch Reaction Water. The importance of being selective in this regard is in order to reduce the set of

included ionic species so as to minimize computational time. The rationale behind their exclusion is that due to their insignificantly low concentrations they have no effect on the system. It must also be noted that the criteria presented below are a starting point and that it is likely that it will be necessary to refine these further (especially considering that inhibitory effects can be significant at parts per billion concentrations).

Criteria for Inclusion of Ionic Species:

1) **Only components with a total concentration of greater than 1 mg/l will be included in the sub-routine.**
2) **Subspecies within a certain system will only be included if they constitute greater than 1% of the total component concentration.**

The ionic speciation model is based on acid-base chemistry and dissolved carbon dioxide chemistry as laid out by Stumm and Morgan (1995). The interfacing of the ionic speciation model with the biological model is achieved via total component concentrations, which are the appropriate quantities to use in material balance calculations. The ionic components represented in the AD-FTRW2 biological model are H^+, $CO_3^=$, NH_4^+, $PO_4^{-=}$, Hx^-, Va^-, Bu^-, Pr^-, Ac^-, Fm^-, Na^+, Cl^- and represent the total concentrations of the ions concerned. These total concentrations are speciated into 28 corresponding ionic species concentrations, from which significant process variables such as alkalinity and pH can be calculated.

Figure 7 on the following page shows the new component setup in AD-FTRW2 and how these components interface with the new ionic speciation routine.

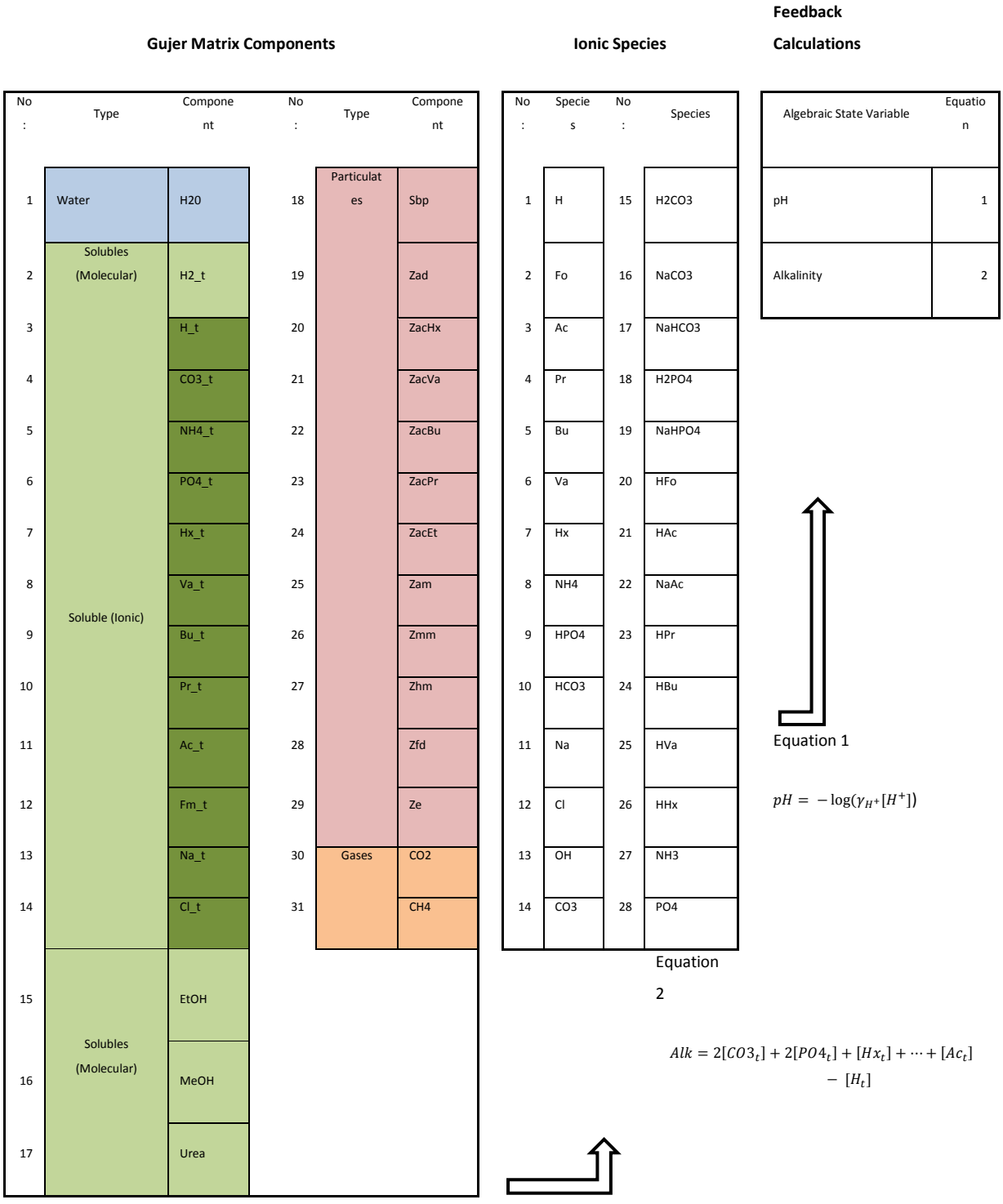

Figure 7: Overview of AD-FTRW2 Model Structure

ii. Carbon Dioxide Expulsion/Dissolution

The process of carbon dioxide expulsion/dissolution is represented in both AD-FTRW1 and AD-FTRW2 by Henry's Law pseudo-equilibrium kinetics. This is an adaptation from the previous implementation in AD-FTRW1 which on close interrogation was deemed to be unrealistic. With reference to section 2.5.3.c.i.1 in the literature review on Gas Exchange, it can be seen that previously, the driving force for the process was defined as a difference between two concentrations ($[H_2CO_3]$ and $[CO_2]$) calculated on the basis of reactor volume as opposed to the difference between the liquid phase concentration of H_2CO_3 and its equilibrium concentration for a defined partial pressure of CO_2 in the gas phase; as is the classical Henry's Law approach. The kinetics for Carbon dioxide expulsion/dissolution were thus reformulated as:

$$r = K_{fCO2}\left([H_2CO_3] - K_h\frac{[CO_2]}{[CO_2]+[CH_4]}\right)$$

Equation 60: AD-FTRW2's carbon dioxide expulsion/dissolution kinetics

Where:

K_h is the Henry's Law constant

$\frac{[CO_2]}{[CO_2]+[CH_4]}$ gives a measure of the partial pressure of CO_2 in the vapour space on the basis that the only gases produced in significant quantities during anaerobic digestion of FTRW are CO_2 and CH_4.

And K_{fCO2} is the kinetic constant for this pseudo-equilibrium formulation and describes how quickly the reaction proceeds towards equilibrium.

The Henry's law constant was sourced from the MinteqA2 database but since it did not have it in the form in which it was applied in AD-FTRW1&2, the constant was calculated from constituent reactions and then adjusted according to the Van't Hoff equation for temperature correction. This was necessary as the constants from the database were for 25°C and the mesophilic anaerobic digester was operated at 37°C.

It was then realised that CO_2 and CH_4 were not the only gases present in the vapour space of the digester. At 37°C, a significant partial pressure of water vapour would exist. This is given by the vapour pressure of water at 37°C and 1 atm and was calculated from the Antoine equation.

This meant that the partial pressure of CO_2 (expressed in the kinetics) had to be adjusted to account for the existence of water vapour in the head-space. The adaptation of the kinetics to account for this phenomenon is shown from the original starting point of pseudo-equilibrium, Henry's Law kinetics:

1) $r = K_{fCO2}\left([H_2CO_3] - K_h p_{CO_2}\right)$
2) $r = K_{fCO2}\left([H_2CO_3] - K_h\frac{[CO_2]}{[CO_2]+[CH_4]}\right)$
3) $r = K_{fCO2}\left([H_2CO_3] - K_h.\left(P_{atm} - p_{H_2O\,(v)}\right).\frac{[CO_2]}{[CO_2]+[CH_4]}\right)$

Where P_{atm} represents $1\,atm$ which is the total pressure of the system and therefore $\left(P_{atm} - p_{H_2O\,(v)}\right)$ represents the partial pressure that can be attributed to CO_2 and CH_4.

Instead of introducing more parameters into the model to account for the partial pressure of water vapour, it was decided to lump these effects into the Henry's law constant:

$$4)\quad K_h^{H_2O(v)} = K_h.\left(P_{atm} - p_{H_2O\,(v)}\right)$$

This yielded the finalized kinetics of:

$$5)\quad r = K_{fCO2}\left([H_2CO_3] - K_h^{H_2O(v)}\frac{[CO_2]}{[CO_2]+[CH_4]}\right)$$

For a full description of the calculations involved in the development of the carbon dioxide expulsion/dissolution kinetics refer to section 7.7 in the appendix.

3.4.4 *Model Configuration: Anaerobic Membrane Bioreactor*

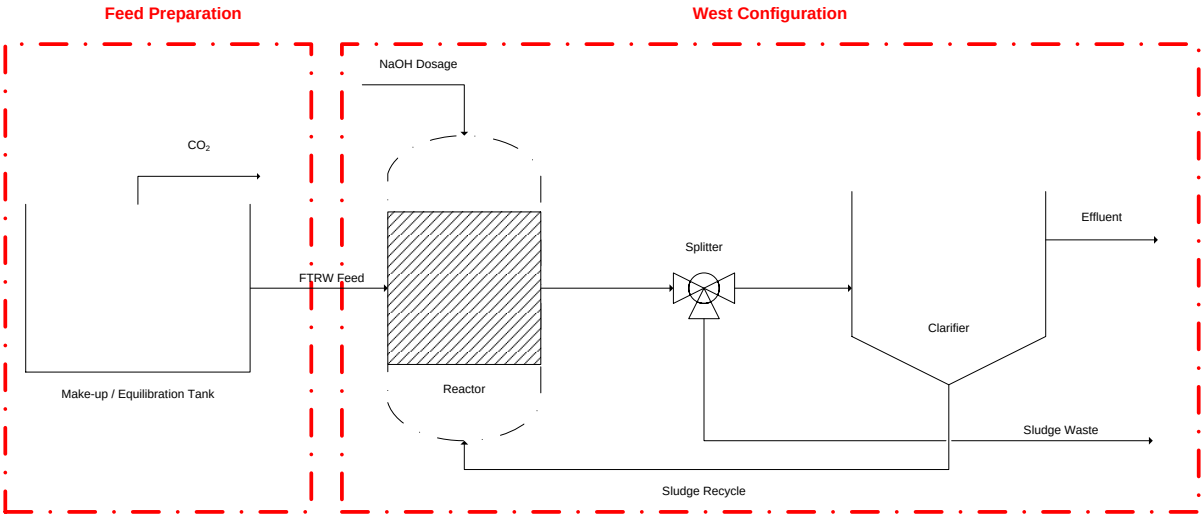

Figure 8: ADFTRW1&2 Model Configuration of lab-scale AnMBR

The above-shown model configuration was applied in AD-FTRW2 to represent the Anaerobic Membrane Bioreactor. The configuration was based on the experimental setup from which the lab-scale data was sourced to validate the model (Figure 9). Notably the configuration is divided into two parts; Feed Preparation and WEST Configuration.

The feed files were prepared based on the experimental data supplied by Van Zyl (2008). In the generation of the experimental data synthetic Fischer-Tropsch reaction water was prepared. It was then dosed with alkalinity to raise the pH to that of actual FTRW (3.77) and conditioned with nutrients to render it amenable to anaerobic digestion. The feed rate, NaOH dosage rates (for pH control) and sludge wastage rates were all recorded and available in the experimental dataset and formed inputs to the models. To prepare the feed files it was

endeavoured to understand the experimental procedures to determine if there were any modelling implications caused by them.

Feed preparation

It was recognized that an equilibration step was required prior to reaction due to the practical consideration that, in the experimental make-up of the synthetic FTRW, alkalinity dosage resulted in a significant liberation of CO_2 prior to the feedstock being fed to the reactor. This meant that the model feed file could not simply be compiled by accounting for all constituents in the synthetic FTRW recipe but also had to account for the loss of CO_2 encountered in its make-up. The equilibration of the feed file was performed externally to the model by calculating the equilibrated mass distribution of the synthetic FTRW with use of the MinteqA2 software.

WEST Configuration

- Experimentally NaOH was dosed as required in order to control reactor pH. This was modelled as a separate input node.
- Experimentally sludge was wasted as required in order to maintain the correct MLSS concentration for optimal membrane performance. Due to the fact that the reactor system is mixed, the sludge waste was modeled as a direct split from the reactor effluent.
- Since the emphasis of this modelling work was placed on the biological and physico-chemical description of the system, it was decided to model the membranes as an ideal splitter. The configuration thus assumes that the membrane system (Figure 9) results in 100% solids retention and was therefore modelled as a clarifier with 100% solids retention and then recycle.

3.5 Model Verification

Model verification was performed by bioprocess atomic balancing and a reaction rate unit consistency check. The process revealed a number of errors or bugs in the programming of the model which were corrected at this point.

Atomic balancing was performed for each bioprocess in the model. Because the process stoichiometry is parameterized by the variable biomass formula and the yield coefficient for the process, atomic balancing was achieved on the basis of a specified biomass formula and yield coefficient. These were specified according to the parameters used to validate the model; a biomass formula of $C_5H_7O_2N$ and the yield coefficient identified for the process during the literature review. C, H, O, N and P balances were then derived and checked according to the conservation of matter.

A reaction rate unit consistency check was then undertaken for each bioprocess. It was checked that all reaction rates were in the units of $\frac{g}{l.d}$.

3.6 Experimental Design

In terms of AD-FTRW2, experimental data required for model validation was sourced from previous lab-scale work done during the development of AD-FTRW1. There was therefore no requirement for experimental design during the course of this study.

3.7 Parameter Estimation and Model Calibration

In reality an Anaerobic Digester being modelled will be subject to a variation in its model parameters due to micro-organism acclimatization, population growth, and feed variations. For a model to be useable, it must be possible to easily update the model parameters. Further to this, a complex design model (such as an AD model) has to be reduced to a point where its parameters can be identified, given available plant data (Olsson and Newell 1999). In this study, parameter estimation was achieved via a comprehensive literature survey and rigorous model calibration techniques were not undertaken. The stoichiometry of each FOG in the dynamic AD-FTRW2 model is dependent on two constants, namely the yield (Y_j) and the unbiodegradable fraction of endogenous biomass (f). Since the dynamic model is time dependent, a second set of kinetic constants is required namely; the maximum specific growth rate (u_{maxj}), the half saturation constant (K_{sj}) and the endogenous decay rate (b). The latter three parameters are required to characterize the process rate equations. In parameter estimation, the values for the stoichiometric and kinetic parameters were identified via a literature survey of the work on which this thesis is a development and are depicted in Table 9 below.

Table 9: Dynamic AD-FTRW2 model constants

		STOICHIOMETRIC		*KINETIC*	
FUNCTIONAL ORGANISM GROUP		*BIOMASS YIELD (Y)*	*ENDOGENOUS RESPIRATION RATE (B)*	*MAXIMUM SPECIFIC GROWTH RATE (μ_{MAX})*	*HALF SATURATION CONSTANTS (K_S)*
		[$mol_{biomass}$/$mol_{substrate}$]	*[1/d]*	*[1/d]*	*[mol/L]*
Acidogenesis	Z_{ad}	0.1074	0.041	0.8	0.00666
Acetogenesis (Hx)	Z_{acHx}	0.0474	0.015	1.18	0.0066
Acetogenesis (Va)	Z_{acVa}	0.0496	0.015	1.53	0.00186
Acetogenesis (Bu)	Z_{acBu}	0.0558	0.015	2.268	0.003125
Acetogenesis (Pr)	Z_{acPr}	0.0376	0.015	1.1	0.01023
Acetogenesis (EtOH)	Z_{acEt}	0.0832	0.015	1.15	0.000128
Acetoclastic Methanogenesis	Z_{am}	0.0157	0.037	1.15	0.0145
Methanol Methanogenesis	Z_{mm}	0.0127	0.037	1.15	0.0145
Hydrogenotrophic Methanogenesis	Z_{hm}	0.004	0.01	1.2	0.0006

Van Zyl (2008)

3.8 Model Validation

To validate AD-FTRW1, a 44 day extract from a 700 day experimental dataset was used. The system was subjected to dynamic flow and load conditions, and no nutrient deficiencies or membrane fouling occurred in this period. The model was then evaluated in terms of the correlation of model predictions versus experimental data with respect to i) alkalinity ii) pH iii) biogas production and iv) effluent SCFA concentration.

3.8.1 *Data Source*

Data needed for the validation of AD-FTRW2 was sourced from the previous study on the development of AD-FTRW1 by Van Zyl (2008). Sampling methods were therefore governed by the previous study's operating procedures and were investigated in order to determine what effects their sampling methods had on the study.

The Dynamic models (AD-FTRW1 and AD-FTRW2) were validated on a dataset generated on an experimental setup designed, built and operated at the UCT water research facilities. The experimental setup consisted of a 23 litre lab-scale Submerged Anaerobic Membrane Bioreactor (AnMBR) treating synthetic Fischer-Tropsch Reaction Water. Experimental data on the various process variables was collected once daily.

A further complication in the experimental dataset was the lack of experimental data between day 25 and day 36 for reactor alkalinity and effluent SCFA concentration. The reason for the missing data was not clear but since this was the only available dataset with which to validate the models, this problem had to be worked around. It must be stated that there were no missing data points for the other measured process variables of pH, biogas production and mixed liquor suspended solids.

a. ***Reactor specifications***

The Submerged AnMBR had a liquid hold up of ~23 L. It included three 200x300 mm (A4-size) submerged Kubota® flat panel ultrafiltration membranes (0.45µm) to achieve effectively 100% solids-liquid-separation. Biogas from the headspace was circulated via a coarse bubble diffuser at a rate of 750 $l/m^2/h$ to sparge the membranes and so reduce fouling. Excess biogas was vented via a water trap release valve and through a cumulative gas meter to monitor biogas production. A critical flux of 4.3 $l/m^2/h$, which could be maintained without specific membrane cleaning procedures, was identified for the system.

The reactor design is illustrated in Figure 9. The reactor shell had three sections; (i) the biogas headspace which has a NaOH dosage point for pH control, (ii) the middle section with effluent collection manifold and FTRW feed point (the membranes were connected via silicon tubing to the effluent manifold), (iii) the bottom section with the membrane housing and a waste line for withdrawing sludge in order to control sludge age.

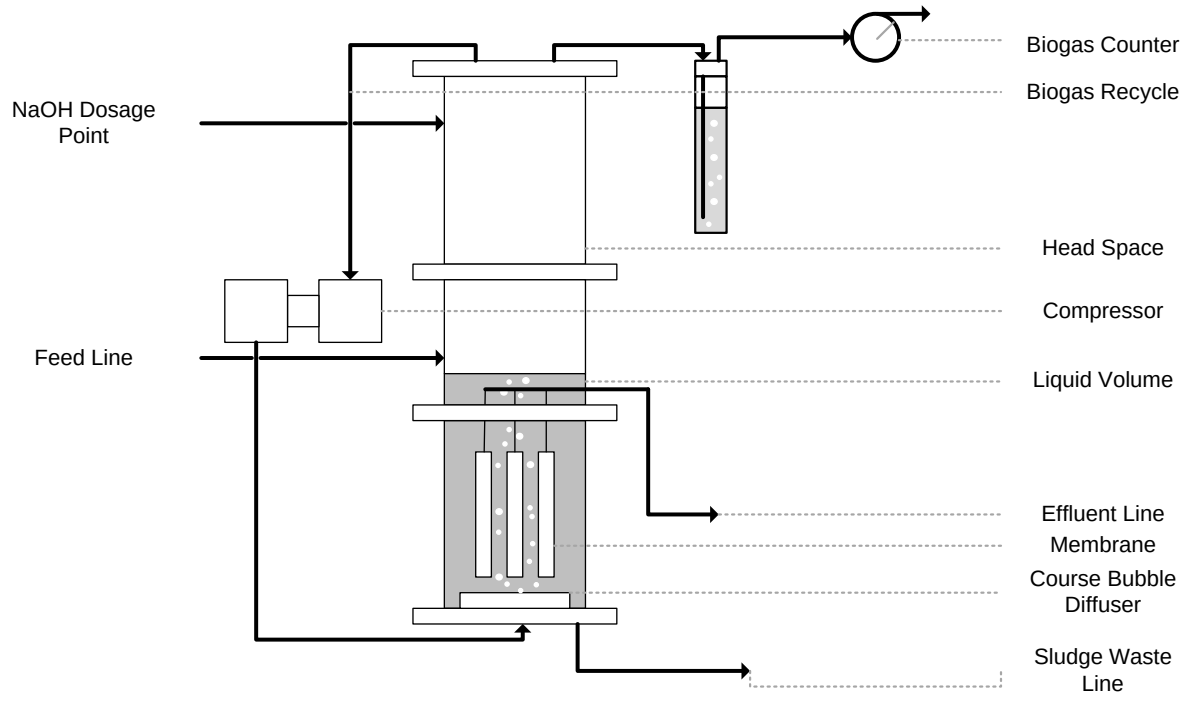

Figure 9: Reactor Setup

b. ***Operating Conditions***

Table 1 shows typical operating conditions that were used.

Table 10: AnMBR Operating Conditions

	OPERATING VARIABLE	***UNIT***	***TYPICAL RANGE***
1	*Feed Flow-rate*	l/d	12-35
2	*Organic Loading Rate*	$kgCOD/m^3_{Vr}/d$	2-25
3	*Sludge Age*	d	60-500
4	*pH*	Dimensionless	6.5 – 7.5
5	*Temperature (mesophilic)*	°C	36-38
6	*Pressure (gauge)*	mmH_2O	20-150

c. ***Feedstock***

The AnMBR was fed a synthetic FTRW consisting of C_2 to C_6 SCFA's, ethanol and methanol and was conditioned with nutrients and some alkalinity (~800 mgCaCO3/L) to render it amenable to anaerobic digestion and to raise the pH to that of actual FTRW (3.77). A study was undertaken to determine the nutrient requirements, and it was shown that N, P, S and Fe were of primary importance in the AD-FTRW system, and were dosed as macro nutrients (~ 50, 10, 4, 1 mg/l_{feed} respectively). Necessary micronutrients included Cu, Zn, Mn, Co, B and Mo (µg/l levels). The only other input was a NaOH solution (100gNaOH/l) which was dosed

directly into the reactor to control pH. The feedstock was prepared in bulk in a make-up tank and then fed to the system as required.

3.8.2 *Selection of initial conditions*

An equivalent set of initial conditions was established for AD-FTRW1 and AD-FTRW2 by using a built-in function in WEST. The modelling software has the functionality to set end values to initial conditions. This effectively copies the state variables at the end of a simulation to the initial conditions for the next simulation. With a random starting set of initial conditions that resulted in a stable simulation (no errors), AD-FTRW2 was run for a long period on a constant feed file. The constant feed file was constructed as the arithmetic mean of the 44 day experimental data set for all inputs. In doing so the model had time to respond to the inputs and traverse towards a more realistic steady-state. The justification for this approach was that the reactor had a predefined range of operating conditions and should the model be run on a typical feed regime for an extended period of time, this should result in reactor state variables that are more representative of the system. Since a full analytical characterization of the reactor contents was not possible this was the best alternative method to establish initial conditions for the integrator. This was successfully achieved for AD-FTRW2 and the initial conditions were then transformed with respect to the different component setup in AD-FTRW1 such that an equivalent set of initial conditions was applied in this model.

3.8.3 *Model Evaluation Approach*

In hypothesis testing, it was decided that structure characterization methods should be used as opposed to goodness-of-fit tests. The justification behind this approach was that these methods provided a means of evaluating model performance based on both model complexity and model accuracy whereas the goodness-of-fit tests reviewed distinguished between the models based solely on model accuracy. It was decided that out of the structure characterization methods, statistical hypothesis testing would be carried out using the F-test modified for model comparison. It was concluded that this test was the only reviewed approach that could determine whether improvement in model performance was a result of a significantly better underlying model or whether the improvement could be attributed to a random occurrence where the dataset was coincidently closer to the predictions of the developed model.

The reviewed F-test for model comparision could not be directly applied to this situation due to the fact that the number of fitted parameters in each model was the same; this leads to zero in the denominator ($p_i - p_j$) of the reviewed F-statistic for model comparison (Equation 33). Instead a variation of the classical F-test to compare distribution variances as laid out by (Davies 1947) was employed. Under the assumption that the model errors ($y_i - f(x_i)$) are normally distributed, an estimate of the variance in each model's prediction errors could be quantified as the sum of squared residuals divided by the model's degrees of freedom. The degrees of freedom are defined as the number of data points less the number of free parameters ($N - p$).

$$s_i{}^2 = \frac{SSR_i}{N - p_i}$$

Equation 61: A measure of variance for model errors

Here some careful definition of "free parameters" is required. Anaerobic Digestion models are highly complex with large numbers of stoichiometric and kinetic parameters. One approach to defining "free parameters" is to regard any constant term in a model as a free parameter. In Anaerobic Digestion models this approach is often not feasible as it places unrealistic demands on the amount of experimental data required to affect a meaningful statistical comparison. With this approach the number of free parameters in AD-FTRW1 and AD-FTRW2 would be in the region of 70. Literature suggests that in order to affect a meaningful comparison the ratio of data-points to parameters ($N:p$) should be at least of the order of 5:1 (Schunn et al., 2005). This means that one would require in excess of 350 days of data (on the basis of one data-point per day) to effect a meaningful comparison. For a system that is prone to periodic upsets and system failure, Anaerobic Digestion modelling does not lend itself to the use of such an ambitious definition of a free parameter. Further to this, it is argued that many of the constants in an Anaerobic Digestion model are theoretical constants that are not altered as part of the model calibration procedure. This is especially true for the integrated ionic speciation modelling which depends on theoretical equilibrium constants. For the abovementioned reasons, a "free parameter" in this research is defined as any parameter that was changed in the calibration of the models. Using this definition, it was necessary to identify which model parameters were adjusted to calibrate the models. For a list of model constants refer to section 7.5 in the appendix.

In this research, parameter estimation was performed via a literature review with special focus on the previous work of van Zyl (2008). As part of this work, the models (AD-FTRW1 and AD-FTRW2) did not undergo a model calibration procedure but instead were validated using the parameters sourced directly from the literature (van Zyl, 2008). The purpose of this study is to discover whether more detailed ionic speciation modelling leads to better pH prediction and for this reason all other elements of the models (AD-FTRW1 and AD-FTRW2) including the model parameters had to be the same. So, in order to discover which parameters were adjusted to calibrate the models, it was necessary to review what was done during the calibration of AD-FTRW1 in the study by van Zyl (2008).

The previous work had applied maximum specific growth rates (μ_{max}) and endogenous decay rates (b_j) for the various FOG's directly from literature. These parameters did not form part of the calibration procedure. This was justified by the fact that variation on these parameters in an anaerobic system is minimal (van Zyl 2008). μ_{max} and b_j for each bioprocess are therefore not regarded as free parameters in this study. With use of WEST's auto-calibration capabilities, a steady-state calibration was performed on the yield coefficients (Y_j) for each FOG. Following this process batch test experimental data was collected to allow for calibration of the half-saturation constants for each FOG (K_{sj}). These calibration steps revealed that only the yield co-efficients and half-saturation constants were adjusted as part of the calibration procedure and, for this reason, they will be regarded as the only free parameters in each model. For 9 biological growth processes in the model, this gave a resultant 18 free parameters in each model on which to base the statistical comparison.

The F-test is then dependant on two quantities; the critical F-value (F_{crit}) which defines the acceptance and rejection regions with respect to the null hypothesis and the F statistic (F_{stat}) which is compared to the critical F-value to draw a conclusion for the hypothesis test. The F-statistic is defined as the ratio of variances between two normal distributions where the larger variance always appears in the numerator (Davies 1947). The F-statistic for this specific case is detailed below.

$$F_{stat} = \frac{s_i^2}{s_j^2} = \frac{\frac{SSR_i}{N - p_i}}{\frac{SSR_j}{N - p_j}}$$

Equation 62: F-statistic

The critical F-value, against which the F-statistic is compared to draw a conclusion on the hypothesis test, is a tabulated quantity that depends on the significance level of the test (α), the degrees of freedom in the numerator ($N - p_i$) of the F-statistic and the degrees of freedom in the denominator ($N - p_j$) of the F-statisitic. These values can easily be sourced from excel with the following calling function:

$$FINV(\alpha, \varphi_N, \varphi_D)$$

Equation 63: Excel calling function for critical F-values

Where:

$\alpha = level\ of\ significance$

$\varphi_N = degrees\ of\ freedom\ in\ the\ numerator$

$\varphi_D = degrees\ of\ freedom\ in\ the\ denominator$

The hypothesis test can then result in two conclusions:

1. If $F_{stat} < F_{crit}$ then the variances are deemed to not be significantly different.
2. If $F_{stat} > F_{crit}$ then the variances are deemed to be significantly different.

Model evaluation did not end at the conclusion of hypothesis testing. Other goodness of fit measures were also selected and calculated in order to quantify the overall performance of each model with respect to the specific dataset used for model validation. While hypothesis testing could evaluate whether these differences were more generally significant, the goodness of fit measures could still quantify these differences with respect to the dataset used for validation and expose underlying characteristics of the models. The goodness of fit measures were selected to evaluate mean error, bias error and to compare model residuals for the specific dataset. For each of these model characteristics (mean error and bias error) both an absolute and a relative criterion were selected to give an indication of error in terms of the measured variables and to enable comparison of errors across target constituents. To evaluate mean error in the models Root Mean Square Error (Equation 34) and Mean Square Relative Error (Equation 36) were selected. The criteria selected to measure bias error were the

absolute measure of Mean Error (Equation 37) and the relative measure of Percentage Bias (Equation 38). Finally the criterion used to compare the residual errors between the models was the Co-efficient of Efficiency (Equation 39) with $\alpha = 1$, $\gamma = 2$, $P_i = ADFTRW2_i$ and the reference model $\tilde{P}_i = ADFTRW1_i$.

4 RESULTS

The results section encompasses the outcomes of model development, comparative model performance and statistical model evaluation.

4.1 Results of Model Development

The results of model development are divided into biological model development and physico-chemical model development. This section then concludes with a summary of the results pertinent to model development.

4.1.1 *Biological Model Development*

The Gujer Matrix representation of AD-FTRW1 (Figure 16 in section 7.6 in the appendix) consists of 27 components and 21 processes. In AD-FTRW2, the Gujer Matrix representation, consists of 31 components and 22 processes. The sources of the increased number of components are phosphate representation, Na^+ and Cl^- () and formate representation (with its associated FOG). OH^- (in AD-FTRW1) is replaced by H_t (in AD-FTRW2) and CO_3_t replaces H_2CO_3 and HCO_3^- in the new Gujer Matrix formulation. You will notice that in AD-FTRW2's Gujer matrix formulation (Figure 10 on the following page) both Na^+ and Cl^- while represented as part of the component list do not take part in any of the processes represented in the Gujer Matrix. It is, however, necessary to include them in the Gujer matrix as it serves as a way of declaring them as variables in WEST since they are used as calculational mechanisms in the ionic speciation routine to fix ionic strength. In terms of the change in number of processes, two extra processes (a growth and a death process) are associated with the newly incorporated formate digestion while process 20 in Figure 16 (hydroxide to bicarbonate) is removed due to the fact that it will be dealt with in the ionic speciation routine in AD-FTRW2. A full representation of the Gujer matrix for AD-FTRW2 is presented on the following A3 page.

Figure 10: Gujer matrix representation of AD-FTRW2

Components

Process	Water	Solubles				
	H_2O	H_2	H^+	CO_3^{2-}	NH_4^+	PO_4^{3-}
Zad Growth	$\frac{Gb\left(\frac{32p-8m+24}{Gb}-4\right)(Y_{ad}-1)}{8}$		$\frac{-Gb\left(\frac{24p-8n+16}{Gb}-3\right)(Y_{ad}-1)}{8}$	$\frac{-Gb\left(\frac{8}{Gb}-2\right)(Y_{ad}-1)}{8}$	$\frac{-n(Y_{ad}-1)}{1}$	$\frac{-p(Y_{ad}-1)}{1}$
Zad Death						
ZacHx Growth	$\left(\frac{2Y_{acHx}}{1}+\frac{Y_{acHx}}{1}\left(\frac{128p-32m+96}{\gamma_b}-\frac{16}{1}\right)-\frac{2}{1}\right)$	$-\left(\frac{2(Y_{acHx}-1)}{1}\right)$	$\left(-\frac{Y_{acHx}}{1}-\frac{Y_{acHx}}{1}\left(\frac{96p-32n+64}{\gamma_b}-\frac{11}{1}\right)+\frac{1}{1}\right)$	$\frac{\left(-Y_{acHx}\left(\frac{32}{\gamma_b}-6\right)\right)}{1}$	$\left(\frac{-32Y_{acHx}n}{\gamma_b}\right)$	$\left(\frac{-32Y_{acHx}p}{\gamma_b}\right)$
ZacHx Death						
ZacVa Growth	$\left(\frac{2Y_{acVa}}{1}+\frac{Y_{acVa}}{1}\left(\frac{104p-26m+78}{\gamma_b}-\frac{13}{1}\right)-\frac{2}{1}\right)$	$\frac{(2(Y_{acVa}-1))}{1}$	$\left(-\frac{Y_{acVa}}{1}-\frac{Y_{acVa}}{1}\left(\frac{78p-26n+52}{\gamma_b}-\frac{9}{1}\right)+\frac{1}{1}\right)$	$\frac{\left(-Y_{acVa}\left(\frac{26}{\gamma_b}-5\right)\right)}{1}$	$\left(\frac{-26Y_{acVa}n}{\gamma_b}\right)$	$\left(\frac{-26Y_{acVa}p}{\gamma_b}\right)$
ZacVa Death						
ZacBu Growth	$\left(\frac{2Y_{acBu}}{1}+\frac{Y_{acBu}}{1}\left(\frac{80p-20m+60}{\gamma_b}-\frac{10}{1}\right)-\frac{2}{1}\right)$	$\frac{(2(Y_{acBu}-1))}{1}$	$\left(-\frac{Y_{acBu}}{1}-\frac{Y_{acBu}}{1}\left(\frac{60p-20n+40}{\gamma_b}-\frac{7}{1}\right)+\frac{1}{1}\right)$	$\frac{\left(-Y_{acBu}\left(\frac{20}{\gamma_b}-4\right)\right)}{1}$	$\left(\frac{-20Y_{acBu}n}{\gamma_b}\right)$	$\left(\frac{-20Y_{acBu}p}{\gamma_b}\right)$
ZacBu Death						
ZacPr Growth	$\left(\frac{3Y_{acPr}}{1}+\frac{Y_{acPr}}{1}\left(\frac{56p-14m+42}{\gamma_b}-\frac{7}{1}\right)-\frac{3}{1}\right)$	$\frac{(3(Y_{acBu}-1))}{1}$	$\left(\frac{-2Y_{acPr}}{1}-\frac{Y_{acPr}}{1}\left(\frac{42p-14n+28}{\gamma_b}-\frac{5}{1}\right)+\frac{2}{1}\right)$	$\frac{\left(1-Y_{acBu}\left(\frac{14}{\gamma_b}-3\right)-Y_{acBu}\right)}{1}$	$\left(\frac{-14Y_{acBu}n}{\gamma_b}\right)$	$\left(\frac{-14Y_{acBu}p}{\gamma_b}\right)$
ZacPr Death						
ZacEt Growth	$\left(\frac{Y_{acEt}}{1}+\frac{Y_{acEt}}{1}\left(\frac{48p-12m+36}{\gamma_b}-\frac{5}{1}\right)-\frac{1}{1}\right)$	$\frac{(2(Y_{acEt}-1))}{1}$	$\left(-\frac{Y_{acEt}}{1}-\frac{Y_{acEt}}{1}\left(\frac{36p-12n+24}{\gamma_b}-\frac{4}{1}\right)+\frac{1}{1}\right)$	$\frac{\left(-Y_{acEt}\left(\frac{12}{\gamma_b}-2\right)\right)}{1}$	$\left(\frac{-12Y_{acEt}n}{\gamma_b}\right)$	$\left(\frac{-12Y_{acEt}p}{\gamma_b}\right)$
ZacEt Death						
Zam Growth	$\left(-\frac{3Y_{am}}{1}+\left(\frac{8Y_{am}(4p-m+3)}{\gamma_b}\right)-\frac{1}{1}\right)$		$\left(\frac{2Y_{am}}{1}-\left(\frac{8Y_{am}(3p-n+2)}{\gamma_b}\right)+\frac{1}{1}\right)$	$\frac{\left(Y_{am}-\frac{8Y_{am}}{\gamma_b}+1\right)}{1}$	$\left(\frac{-8Y_{am}n}{\gamma_b}\right)$	$\left(\frac{-8Y_{am}p}{\gamma_b}\right)$
Zam Death						
Zmm Growth	$\left(\frac{Y_{mm}}{1}\left(\frac{24p-6m+18}{\gamma_b}-2\right)-\frac{Y_{mm}}{4}+\frac{1}{4}\right)$		$\left(\frac{1}{2}-\frac{Y_{mm}}{1}\left(\frac{18p-6n+12}{\gamma_b}-\frac{2}{1}\right)-\frac{Y_{mm}}{2}\right)$	$\left(\frac{1}{4}-\frac{Y_{mm}}{1}\left(\frac{6}{\gamma_b}-1\right)-\frac{Y_{mm}}{4}\right)$	$\left(\frac{-6Y_{mm}n}{\gamma_b}\right)$	$\left(\frac{-6Y_{mm}p}{\gamma_b}\right)$
Zmm Death						
Zhm Growth	$\left(\left(\frac{Y_{hm}(8p-2m+6)}{\gamma_b}\right)-\frac{3Y_{hm}}{4}+\frac{3}{4}\right)$	(-1)	$\left(\frac{Y_{hm}}{2}-\left(\frac{Y_{hm}(6p-2n+4)}{\gamma_b}\right)-\frac{1}{2}\right)$	$\left(\frac{Y_{hm}}{4}-\frac{2Y_{hm}}{\gamma_b}-\frac{1}{4}\right)$	$\left(\frac{-2Y_{hm}n}{\gamma_b}\right)$	$\left(\frac{-2Y_{hm}p}{\gamma_b}\right)$
Zhm Death						
Zfd Growth	$\left(Y_{fd}+Y_{fd}\left(\frac{8p-2m+6}{\gamma_b}-1\right)-1\right)$	$\frac{(1-Y_{fd})}{1}$	$\left(-\frac{Y_{fd}}{1}-\frac{Y_{fd}}{1}\left(\frac{6p-2n+4}{\gamma_b}-\frac{1}{1}\right)+\frac{1}{1}\right)$	$\left(\frac{1}{1}-\frac{Y_{fd}}{1}\left(\frac{2}{\gamma_b}-1\right)-\frac{Y_{fd}}{1}\right)$	$\left(\frac{-2Y_{fd}n}{\gamma_b}\right)$	$\left(\frac{-2Y_{fd}p}{\gamma_b}\right)$
Zfd Death						
CO2 Exp_Diss	$(+1)$		(-2)	(-1)		
Urea Hydrolysis	(-2)			$(+1)$	$(+2)$	

Process	Solubles										
	Hx^-	Va^-	Bu^-	Pr^-	Ac^-	Fm^-	Na	Cl	EtOH	MeOH	Ur
Zad Growth					$\left(\frac{-Gb(Y_{ad}-1)}{8}\right)$						
Zad Death											
ZacHx Growth	(-1)		$\frac{(1-Y_{acHx})}{1}$		$\frac{(1-Y_{acHx})}{1}$						
ZacHx Death											
ZacVa Growth		(-1)		$\frac{(1-Y_{acVa})}{1}$	$\frac{(1-Y_{acVa})}{1}$						
ZacVa Death											
ZacBu Growth			(-1)		$\frac{(2(1-Y_{acBu}))}{1}$						
ZacBu Death											
ZacPr Growth				(-1)	$\frac{(1-Y_{acPr})}{1}$						
ZacPr Death											
ZacEt Growth					$\frac{(1-Y_{acEt})}{1}$				(-1)		
ZacEt Death											
Zam Growth					(-1)						
Zam Death											
Zmm Growth										(-1)	
Zmm Death											
Zhm Growth											
Zhm Death											
Zfd Growth						(-1)					
Zfd Death											
CO2 Exp_Diss											
Urea Hydrolysis											(-1)

Process	Particulates												Gases	
	Sbp	Z_{ad}	Z_{acHx}	Z_{acVa}	Z_{acBu}	Z_{acPr}	Z_{acEt}	Z_{am}	Z_{mm}	Z_{hm}	Z_{fd}	Z_e	CO_2	CH_4
Zad Growth	(-1)	Y_{ad}												
Zad Death	$\frac{(1-f)}{1}$	(-1)										f		
ZacHx Growth			$\left(\frac{32Y_{acHx}}{\gamma_b}\right)$											
ZacHx Death	$\frac{(1-f)}{1}$		(-1)									f		
ZacVa Growth				$\left(\frac{26Y_{acVa}}{\gamma_b}\right)$										
ZacVa Death	$\frac{(1-f)}{1}$			(-1)								f		
ZacBu Growth					$\left(\frac{20Y_{acBu}}{\gamma_b}\right)$									
ZacBu Death	$\frac{(1-f)}{1}$				(-1)							f		
ZacPr Growth						$\left(\frac{14Y_{acPr}}{\gamma_b}\right)$								
ZacPr Death	$\frac{(1-f)}{1}$					(-1)						f		
ZacEt Growth							$\left(\frac{12Y_{acEt}}{\gamma_b}\right)$							
ZacEt Death	$\frac{(1-f)}{1}$						(-1)					f		
Zam Growth								$\left(\frac{8Y_{am}}{\gamma_b}\right)$						$\frac{(1-Y_{am})}{1}$
Zam Death	$\frac{(1-f)}{1}$							(-1)				f		
Zmm Growth									$\left(\frac{6Y_{mm}}{\gamma_b}\right)$					$\frac{\left(\frac{3}{4}-\frac{3Y_{mm}}{4}\right)}{1}$
Zmm Death	$\frac{(1-f)}{1}$								(-1)			f		
Zhm Growth										$\left(\frac{2Y_{hm}}{\gamma_b}\right)$				$\frac{\left(\frac{1}{4}-\frac{Y_{hm}}{4}\right)}{1}$
Zhm Death	$\frac{(1-f)}{1}$									(-1)		f		
Zfd Growth											$\left(\frac{2Y_{fd}}{\gamma_b}\right)$			
Zfd Death	$\frac{(1-f)}{1}$										(-1)	f		
CO2 Exp_Diss													$(+1)$	
Urea Hydrolysis														

Figure 10: Gujer matrix representation of AD-FTRW2

4.1.2 *Physico-chemical model development*

The most significant part to the physico-chemical model development included the development of the equilibrium based ionic speciation subroutine that enabled detailed modelling of SCFA dissociation, the carbonate system, the phosphorous system and the ammonia system. Development was then focused on the accurate representation of carbon dioxide expulsion/dissolution kinetics. Refer to section 7.9 in the appendix for the detailed code of the ionic speciation sub-routine.

4.1.3 *Summary of Results for Model Development*

The table below shows a comparison of the model features in AD-FTRW1 and AD-FTRW2. The differences reflect the results of the model development performed during the course of this study.

Table 11: Comparison of features in the AD-FTRW1 and AD-FTRW2 models

	AREA OF DIFFERENCE	*AD-FTRW1*	*AD-FTRW2*
1	*Implementation of Ionic Speciation Chemistry*	Integrated into bioprocess stoichiometry	Speciation sub-routine
		Equilibrium based	Equilibrium Based
2	*Acid/base chemistry*	SCFA dissociation	SCFA dissociation
		Carbonate system	Carbonate system
		Ammonia system	Ammonia system
			Phosphorous system
3	*pH range of applicability*	6.5 – 7.5	3.5 – 9.0
4	*Biomass Formula*	Fixed	Variable (parameterized)
		$C_5H_7O_2N$	$C_kH_lO_mN_nP_p$
5	*Phosphorous uptake*	Not considered	Represented
6	*Formate Digestion*	Not considered	Represented

4.2 Comparative Model Performance

In addressing the research hypothesis, this part of the results section explores the efficacy of the two different approaches adopted in AD-FTRW1&2 to integrating the physico-chemical speciation processes with the biological model. Through a comparative model performance exercise an assessment is made as to whether the revised approach to physico-chemical integration (in AD-FTRW2) has resolved the shortcomings experienced in the preliminary approach (in AD-FTRW1).

The comparison of AD-FTRW1 vs AD-FTRW2 was performed with the rationale that all elements of AD-FTRW1 should be left unchanged besides the handling of physico-chemical modelling. For this reason, all of the abovementioned features (in Table 11) besides those directly related to physico-chemical modelling were "switched off/equated" to effect a just comparison. In other words the biomass formula was set to $C_5H_7O_2N$ in both models (automatically removing phosphorous uptake in AD-FTRW2) and formate digestion was excluded from the bioprocesses.

To compare AD-FTRW1 and AD-FTRW2, a 44 day extract from a 700 day experimental dataset was used. The system was subjected to dynamic flow and load conditions, and no nutrient deficiencies or membrane fouling occurred in this period. The models have been evaluated in terms of the correlation of model predictions versus experimental data with respect to i) alkalinity ii) pH iii) biogas production iv) effluent SCFA concentration and v) mixed liquor suspended solids. It must be noted that, due to the fact that the experimental data was sourced from a different study, confidence intervals could not be determined for the experimental data. It was assumed that the experimental data was accurate.

In terms of computational time AD-FTRW1 was significantly faster than AD-FTRW2 in its simulations. Speeds were dependent on the type of integrator used and results for two integrator types are presented in the table below for the 44 day simulation.

Table 12: Comparative Model Computational Speeds

MODEL	*INTEGRATOR*		
	CVODE		*RK4ASC*
	STIFF	*NON-STIFF*	
AD-FTRW1	28.9 s	9 min 08 s	1 min 23 s
AD-FTRW2	2 min	7 min 32 s	2 min 40 s

It must be noted that the models were initialized with equivalent conditions, as far as possible given the different model components. The biomass and substrate components are substantially the same, however the ionic compositions could not be made identical due to the different component frameworks. In relation to this it was decided to present all simulated results from day 2 onwards, as the initial assumptions were too influential on the initial parts of the simulations.

The results of the comparisons are detailed below.

4.2.1 *pH: AD-FTRW1 vs AD-FTRW2*

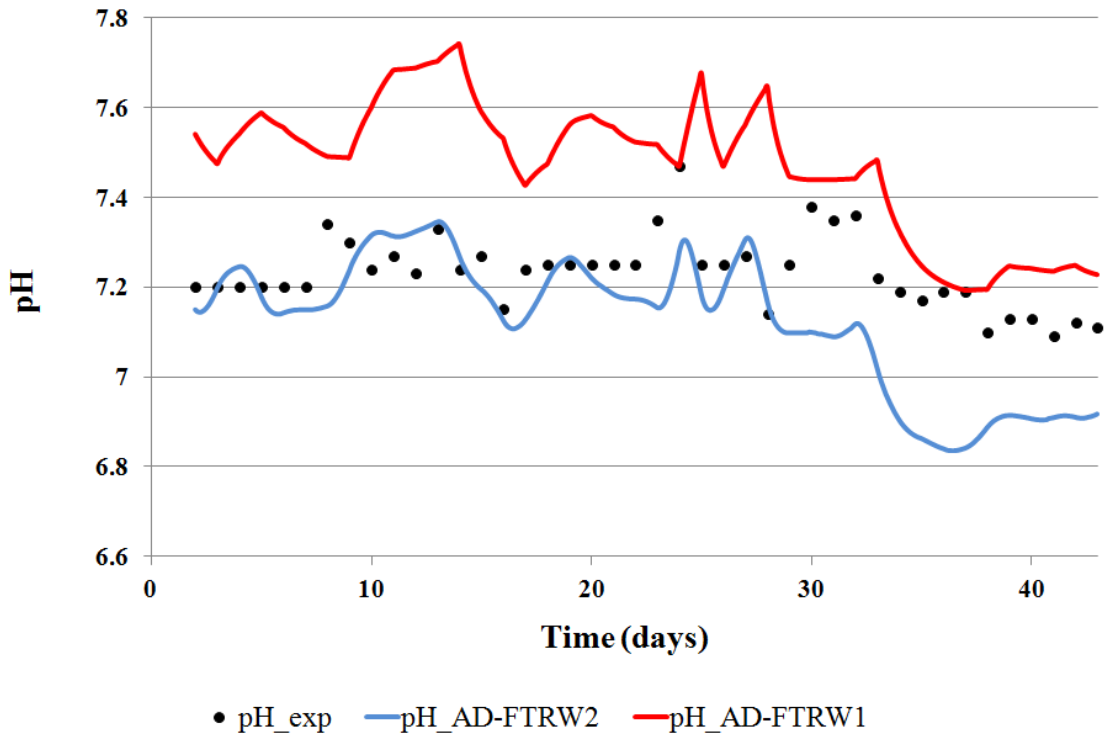

Figure 11: pH

AD-FTRW1 presents a root mean squared error (RMSE) on pH of 0.27 as opposed to 0.16 in AD-FTRW2. From a quantitative perspective this translates into a 40% improvement in pH prediction. A percentage bias (PBIAS) of -3.27% in AD-FTRW1 and 1.5% in AD-FTRW2 is indicative of systematic over-prediction and under-prediction respectively. The small values of percentage bias indicate that bias error should not be a problem in pH prediction for either of the models. Hypothesis testing carried out on pH revealed that AD-FTRW2 produced a significantly better fit to the data at a 95% confidence level.

4.2.2 *Alkalinity: AD-FTRW1 vs AD-FTRW2*

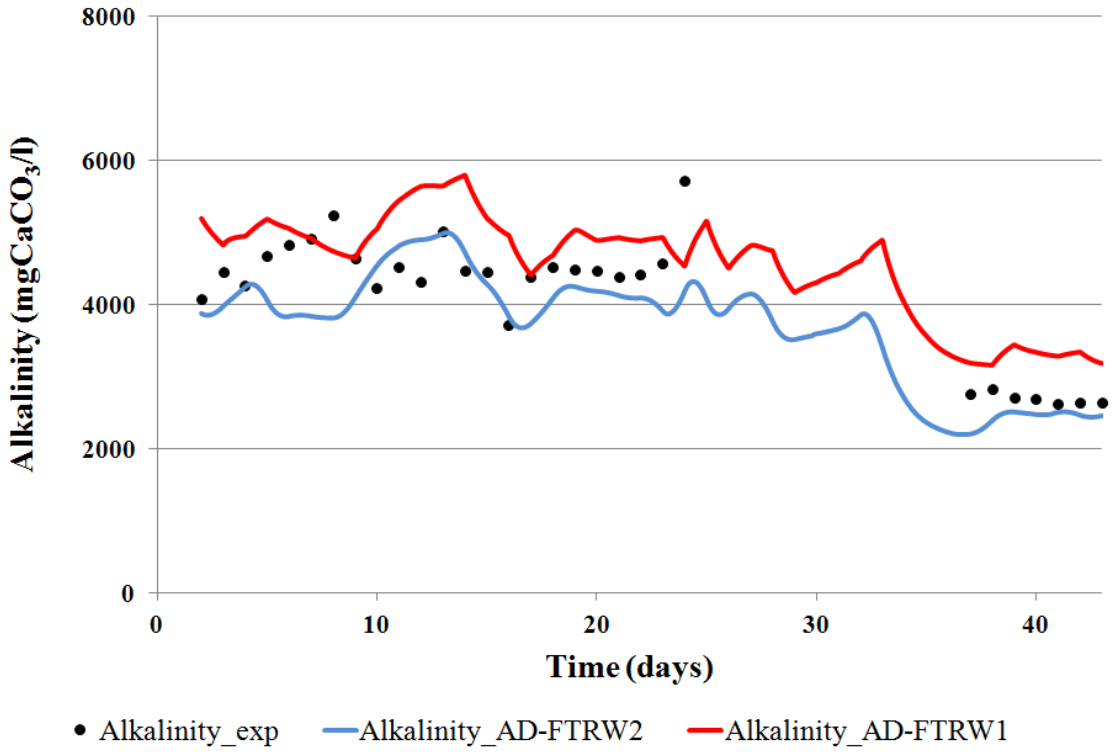

Figure 12: Alkalinity

The models both describe experimental reactor alkalinity closely. AD-FTRW2 performs better in this area with a root mean squared error (RMSE) of 611.54 vs that of 690.20 $mgCaCO_3/l$ in AD-FTRW1. The reason for the lack of experimental data between day 25 and day 36 is that alkalinity was not measured over that period. The same is true for effluent SCFA concentration over the same period below. As was the case with pH prediction, percentage bias (PBIAS) reveals that AD-FTRW1 systematically over-predicts by approximately 10% in the area of reactor alkalinity while AD-FTRW2 systematically under-predicts by a similar amount for the same variable. Hypothesis testing revealed that although AD-FTRW2 performs better in predicting alkalinity on this data set, the difference is not statistically significant.

4.2.3 *Effluent SCFA Concentration: AD-FTRW1 vs AD-FTRW2*

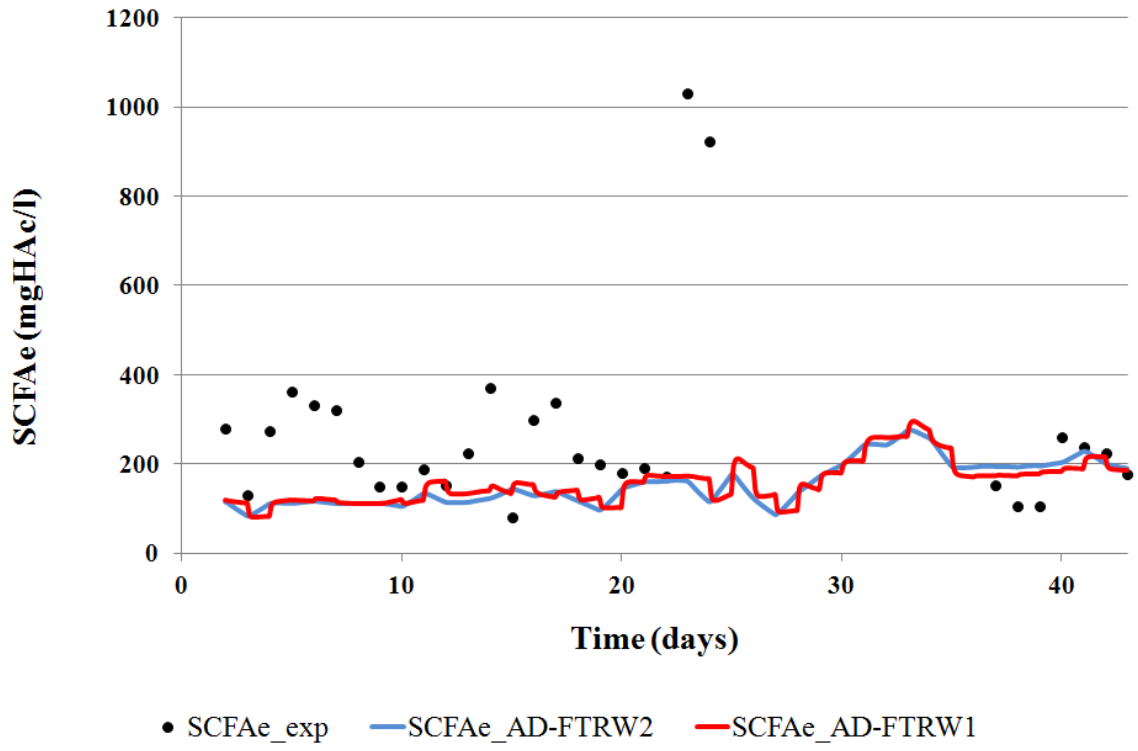

Figure 13: Effluent SCFA Concentration

Both models predict the effluent SCFA concentrations very similarly. The root mean squared error (RMSE) of AD-FTRW1&2 on effluent SCFA concentration are 237.97 and 243.49 mgHAc/l respectively. This is in line with the visually apparent closeness of the models to one another. AD-FTRW1 predicts this variable marginally better than AD-FTRW2. Both models systematically under-predict this process variable with a percentage bias (PBIAS) of approximately 48% for AD-FTRW1 and 44% for AD-FTRW2.

The apparent difference in smoothness of the two curves is simply a function of the plot precision used in the recording of this data. It is not dependent on any differences in model formulation or integrator settings and does not influence the calculation of any of the statistical properties since these are based on the point value of the model at the same time as each experimental point.

4.2.4 *Biogas Production: AD-FTRW1 vs AD-FTRW2*

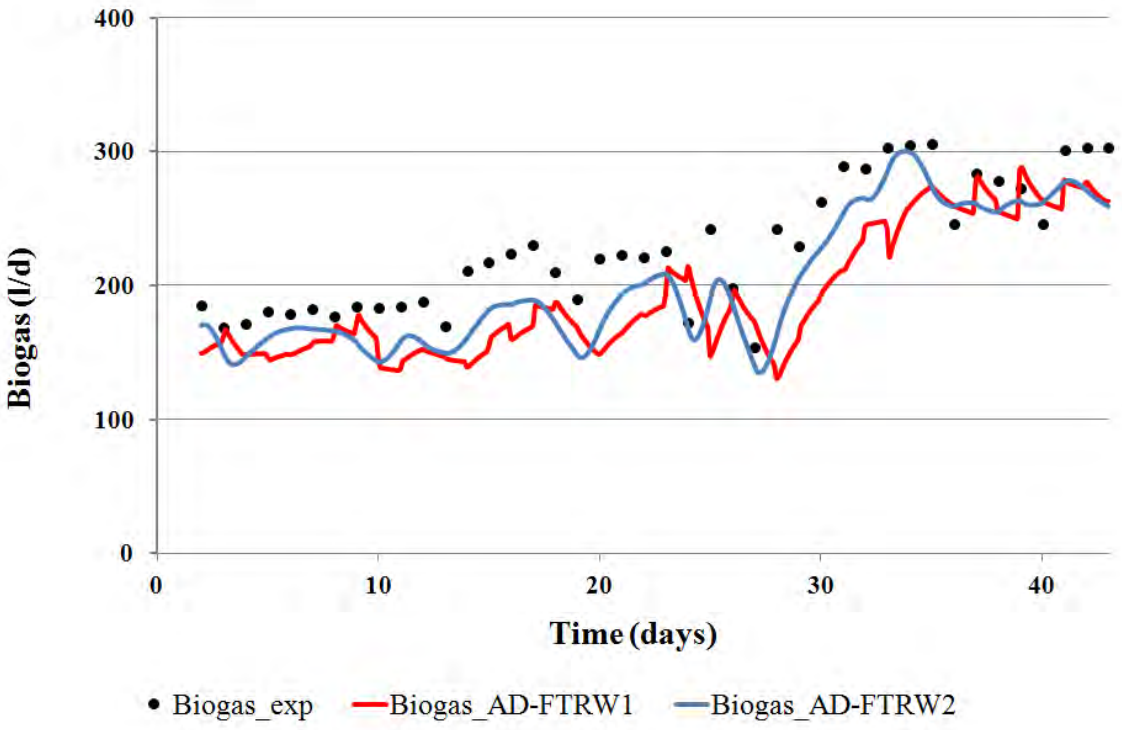

Figure 14: Biogas Production

Modelled biogas production correlates well with the experimentally measured data. AD-FTRW2 performs best in predicting this process variable with a root mean squared error (RMSE) of 41.35 l/d. AD-FTRW1 shows a root mean squared deviation of 54.6 l/d. This is indicative of a 25% improvement on biogas prediction. Although a marked improvement in the predictive capacity of the model with respect to this variable, statistical hypothesis testing indicates that the improvement is not significant at a 95% confidence level. It is visually apparent that both AD-FTRW1 and AD-FTRW2 systematically under-predict biogas prediction with percentage bias values of 21% and 16% respectively. Another interesting observation is that the profiles generated by both models are very similar however AD-FTRW2 tends to lead AD-FTRW1 in responding to changes in the data. The reason for this is not clear but it may be related to the kinetic approach to some speciation processes in AD-FTRW1 as opposed to the equilibrium approach applied comprehensively to AD-FTRW2.

4.2.5 *Mixed Liquor Suspended Solids: AD-FTRW1 vs AD-FTRW2*

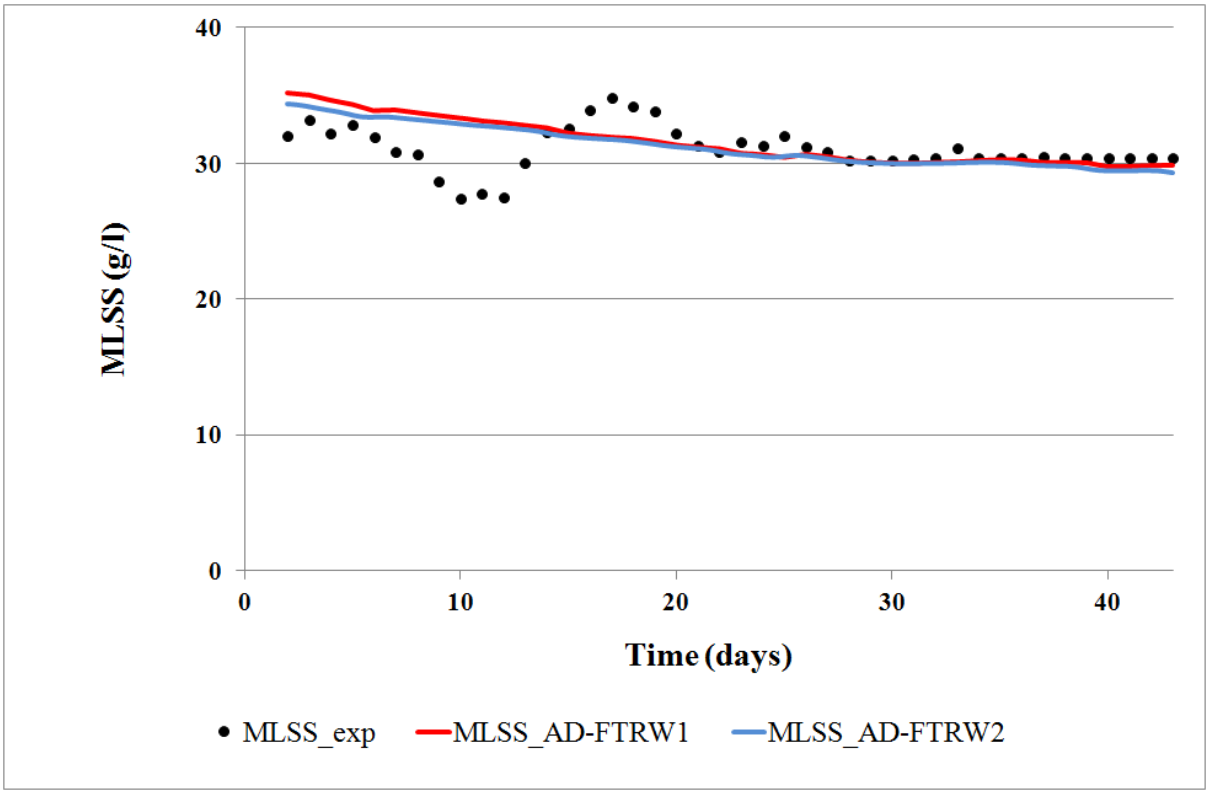

Figure 15: Mixed Liquor Suspended Solids

As with effluent SCFA concentration, both AD-FTRW1 and AD-FTRW2 show very similar correspondences with the experimental mixed liquor suspended solids data. The root mean squared errors on this variable were 2.16 g/l for AD-FTRW1 and 1.98 g/l for AD-FTRW2. Percentage bias values in the region of -2% for AD-FTRW1 and -1% for AD-FTRW2, indicate that both models display very little bias error on this variable in the dataset. The marginal improvement in AD-FTRW2's performance on this variable as compared to AD-FTRW1 is not significant at a 95% confidence level.

4.3 Model Evaluation

In distinguishing between the performance of AD-FTRW1 and AD-FTRW2, conclusions as to the significance of their differences were drawn from the F-test method of hypothesis testing. Various other goodness-of-fit measures were also used to analyze the performance of AD-FTRW1 and AD-FTRW2 on this specific dataset. The results from these analyses are represented in the tables below.

Table 13: Model Evaluation Goodness-of-fit Measures

		Goodness-of-fit Absolute Criteria			
Model Characteristic		***Mean Error***		***Bias Error***	
Statisitcal Index		***RMSE***		***ME***	
Output	*Unit*	*AD-FTRW1*	*AD-FTRW2*	*AD-FTRW1*	*AD-FTRW2*
pH	-	0.27	0.16	-0.24	0.11
Alkalinity	*[mgCaCO3/L]*	690.20	611.54	-484.95	375.46
Biogas Flow Rate	*[L/d]*	54.60	41.35	47.24	35.76
VFAe	*(mgHAc/l)*	237.97	243.49	130.99	119.25
MLSS	*g/l*	2.16	1.98	-0.57	-0.25

		Goodness-of-fit Relative Criteria				
Model Characteristic		***Mean Error***		***Bias Error***		***Model Comparison***
Statisitcal Index		***MSRE***		***PBIAS***		$CE_{1,2}$
Output	*Unit*	*AD-FTRW1*	*AD-FTRW2*	*AD-FTRW1*	*AD-FTRW2*	*AD-FTRW1vs2*
pH	-	0.0014	0.0005	-3.27	1.50	0.65
Alkalinity	-	0.03	0.02	-11.78	9.12	0.21
Biogas Flow Rate	-	0.06	0.03	20.95	15.86	0.43
VFAe	-	0.26	0.29	48.61	44.26	-0.05
MLSS	-	0.0054	0.0045	-1.84	-0.81	0.16

For each model characteristic (Mean Error and Bias Error), an absolute and a relative criterion were selected to quantify these characteristics. This allows one to understand the characteristics in terms of the units of the measured variable via the absolute criteria and then allows comparison of these characteristics across variables via the relative criteria.

As can be seen in the above table, according to the root mean squared error index (RMSE), the revised model (AD-FTRW2) performs more accurately in predicting all of the model outputs investigated except for the effluent Short Chain Fatty Acid concentration (VFAe). Notably (on the basis of RMSE) there is approximately a 40% improvement in pH prediction accuracy and a 25% improvement in biogas production prediction. Mean Square Relative Error (MSRE), also a measure of mean error but in relative terms, shows that both models are most accurate in predicting pH and least accurate in predicting VFAe. The hierarchy in accuracy for both models according to MSRE from most accurately modelled to least accurately modelled is pH > MLSS > Alkalinity > Biogas Flow Rate > VFAe.

Bias error in each of the models for the given dataset was quantified with the Mean Error (ME) and Percentage Bias (PBIAS) criteria. On the basis that measures of error in these criteria are defined as observed variable less predicted variable, a negative outcome reflects a systematic over-prediction and a positive outcome reflects a systematic under-prediction. AD-FTRW2 under-predicts all of the measured variables except Mixed Liquor Suspended Solids (MLSS) which is marginally over-predicted. Due to the very low percentage bias outcomes for both pH and MLSS in AD-FTRW2, it can be said that the model displays negligible bias error for these variables. Bias error can be said to be significant in AD-FTRW2 for the variables Alkalinity, Biogas Flow Rate and VFAe. Notably bias error for pH and Alkalinity shifts from systematic over-prediction in AD-FTRW1 to systematic under-prediction in AD-FTRW2. This indicates a marked change in the underlying models governing these variables. These variables would be most significantly influenced by the ionic speciation modelling in AD-FTRW1 and AD-FTRW2 which is the area that this study has changed most markedly.

Finally the co-efficient of efficiency ($CE_{1,2}$) gives a means of directly comparing the performance of each of the models on the given dataset with a value of 1 indicating perfect performance (with respect to AD-FTRW2), zero indicating no improvement in performance from the reference model and negative values indicating negative improvement with respect to the reference model. The reference model in this instance was taken as AD-FTRW1. The co-efficient of efficiency highlights that AD-FTRW2 presented an improved performance on all of the measured variables except VFAe with the greatest area of improvement being in the area of pH prediction.

Table 14: Hypothesis Test Parameters

			Hypothesis Testing			
Statisitcal Index		***Degrees of Freedom***	***Sum of Squared Residuals***		***Measure of Variance***	
Output	*Unit*	*AD-FTRW1&2*	*AD-FTRW1*	*AD-FTRW2*	*AD-FTRW1*	*AD-FTRW2*
pH	-	26	3.25	1.15	0.13	0.04
Alkalinity	-	14	15244100.60	11967520.50	1088864.33	854822.89
Biogas Flow Rate	-	26	131161.07	75241.52	5044.66	2893.90
VFAe	-	14	1812185.57	1897193.05	129441.83	135513.79
MLSS	-	26	205.19	172.21	7.89	6.62

With reference to the methodology outlined in Section 3.8.2, a hypothesis test was carried out by means of an F-test to establish whether the improvements seen in the predictive capacity of AD-FTRW2 were significant as compared to the predictions of AD-FTRW1. The test hinges on a ratio of two variances which were calculated as the quotient of the sum of squared residuals over degrees of freedom. All of these measures are depicted in Table 14 above. Two important notes are the differing degrees of freedom between the modelled variables and the fact that the sum of squared residuals is reduced from AD-FTRW1 to AD-FTRW2 for all variables except VFAe. The implication of the latter was that the F-test was not performed on VFAe due to the fact that there was clearly no improvement on the predictability of this variable. The degrees of freedom are calculated as the difference between the number of data points

and the number of free parameters in each model ($N - p$). The reason for the fact that this quantity alternates between 26 and 14 for the different variables is that the dataset used for model validation had 12 days of data missing for alkalinity and effluent volatile fatty acid concentration.

Table 15: Hypothesis Test Conclusions

		Hypothesis Testing		
Statisitcal Index		***F-test statistic***	***Critical F Value***	***F-test conclusion***
Output	*Unit*	*AD-FTRW1 vs 2*	*AD-FTRW1 vs 2*	*AD-FTRW1 vs 2*
pH	-	2.83	1.93	significantly_different
Alkalinity	-	1.27	2.48	not_significantly_different
Biogas Flow Rate	-	1.74	1.93	not_significantly_different
VFAe	-			
MLSS	-	1.19	1.93	not_significantly_different

Table 15 above depicts the results of the hypothesis test on each target constituent. It was carried out at a significance level of $\boldsymbol{\alpha = 0.05}$. The F-test, which takes into account model complexity together with model accuracy, reveals that AD-FTRW2 is only significantly better in predicting pH. Under the assumptions highlighted in the section on Model Evaluation Approach, the statistical analysis supports the research hypothesis that **"The pH prediction in Sasol Technology's existing AD model (AD-FTRW1) will be improved through the incorporation of a more comprehensive ionic speciation model (AD-FTRW2)."**

5 DISCUSSION

Anaerobic digestion, as a treatment option, has significant operational and cost benefits when compared to an activated sludge unit treating a similar effluent. These include reduced energy input, energy recovery from biogas and low sludge production.

Reduced energy input (as compared to activated sludge systems) is as a consequence of the fact that anaerobic digestors do not require aeration. Aeration is coupled with a significant energy cost due to the fact that it requires blowers to force air into the system. In the Sasol wastewater treatment processes it is also speculated that aeration results in volatilization of many of the organics in the wastewater. This is an environmental concern as it implies a displacement of the contaminants in the wastewater whereby water pollution becomes air pollution with no intermediate treatment.

Lower sludge production is a consequence of the fact that biomass yield co-efficients are lower in anaerobic systems. Further to this, anaerobic membrane bioreactors (the reactor technology for which AD-FTRW1 and AD-FTRW2 were specifically developed), have an increased advantage in that they have a significantly reduced land footprint. This stems from the fact that the membrane systems enable increased sludge retention times resulting in better acclimated biomass that is more efficient in digesting the organics typically present in that system's feedstock. This increase in digestion efficiency leads to a reduction in the required hydraulic retention times and therefore smaller reactors. As was mentioned previously the drawbacks to anaerobic digestors are that they are difficult to control, prone to system failure and they lack disturbance rejection ability. The solution to these drawbacks is seen to lie in accurate mathematical modelling of these systems that will lead to advanced model-based process control. It is in light of this philosophy that this research was undertaken and the implications of the steps taken in this research are discussed in greater detail in this section.

The enhanced modelling depicted by the comparative results of AD-FTRW1 versus AD-FTRW2 has industrial implications in the realms of research and development, process design, operation and control.

- Coupled modeling and experimentation in the context of optimal experimental design has the potential to speed the technological development process in this field.
- The enhanced process model (AD-FTRW2) could assist in the design of new anaerobic digestion of Fischer-Tropsch reaction water facilities.
- From an operation and control perspective, AD-FTRW2 could assist in advanced model-based control to improve process disturbance rejection. Further to this, the model could be used to optimize alkalinity and nutrient dosage, which has proven to be the major operating cost in anaerobic digestion of Fischer-Tropsch reaction water.

The significance of this work from a research perspective in the anaerobic digestion modelling field is that the developed model (AD-FTRW2) addresses limitations identified in preceding AD models and

specifically in ADM1. The enhanced physico-chemical modelling achieved by integrating a comprehensive ionic speciation subroutine introduces the modelling of non-ideality through ion activity corrections and ion pairing; both model features that were lacking in ADM1 (Batstone et al., 2012). The validation of AD-FTRW2 on experimental data sourced from a lab-scale digester treating industrial effluent of a pH of approximately 3.77 shows that the method of physico-chemical modelling applied in this research gives indications of representing low pH systems well. This should improve the capability of the model for simulating digester failure; a limitation identified in ADM1 whose pH system is only valid for dilute systems (Batstone et al., 2012). While the better modelling of digester failure is indicated, this needs to be validated with appropriate reactor failure experimental data that was not available in this research. AD-FTRW2 is also significant in that it shows a strong interaction between gas transfer (carbon dioxide expulsion and dissolution), ionic speciation and consequently pH in its modelling results. The interaction of these systems is known to be significant (Batstone et al. 2012) but is not always modelled as such. Finally, AD-FTRW2 handles the modelling of the phosphorous weak acid-base system; another limitation identified in ADM1.

5.1 Accounting for higher organic acids in the speciation sub-routine

In comparing the modelling approaches of AD-FTRW1 versus AD-FTRW2, it is seen that AD-FTRW1 built kinetic considerations and speciation chemistry into the biological process stoichiometry. In contrast, AD-FTRW2 adopts the philosophy of keeping speciation chemistry and bioprocess stoichiometry separate but interactive through its ionic speciation sub-routine. Apart from the apparent performance advantages depicted in the results section, another advantage of this approach is that in the event of a modelling errors/inaccuracies the root of the error will be easier to find as the model structure is not as convoluted.

In developing the ionic speciation sub-routine, a problem was encountered in the sourcing of information on the ionic interactions across weak acid/base subsystems for the longer chain SCFA's (valerate and hexanoate). The trend in the equilibrium constants from acetate to hexanoate was investigated in order to draw some conclusions as to how the longer chain SCFA's speciation behaviour would possibly compare to the shorter chain SCFA's (acetate, propionate and butyrate) for which comprehensive speciation data was available. It was noticed that the equilibrium constants for the various acids in the homologous series tended to level out after propionate (refer to Figure 17 in the appendix). On the basis of this investigation it was assumed that the longer chain fatty acids (valerate and hexanoate) would behave similarly to butyrate (the longest SCFA for which comprehensive speciation data was available) from an ionic speciation perspective. For the purposes of the ionic speciation sub-routine these acids were lumped together and treated as if they were all butyrate. It must be noted that even though these components were lumped together in the ionic speciation sub-routine, for the purposes of the integration of the bioloigical processes they remained independent.

5.2 Factors influencing validity of the comparison between the two models

Once AD-FTRW2 was built, a number of modelling considerations had to be accounted for before a fair comparison could be effected between AD-FTRW1 and AD-FTRW2. The feed files for the models had to be prepared and a set of equivalent initial conditions had to be determined such that the integration could proceed and such that both models began at a similar state.

5.2.1 *Equilibration of feedstock*

The models (AD-FTRW1 and AD-FTRW2) were run with both the equilibrated feed files and the non-equilibrated feed files to investigate the effect of this consideration on the models performance. The results of both models on the basis of the non-equilibrated feed files reflected elevated biogas production rates (caused by the increased liberation of carbon dioxide within the system) and lower pH predictions. Fundamentally, the correct modelling approach was to run the models on the equilibrated feed files as was discussed in Section 3.4.4 and these are the only results that are presented in the thesis. Both models' performances were generally improved by the equilibration of the feed files. This was especially true for pH prediction. This process highlighted the importance of investigating sampling methods and quantifying their effect on experimental data.

5.2.2 *Missing experimental data*

In model evaluation on alkalinity and effluent SCFA concentration, the missing data was handled by basing the statistical criteria on the periods for which there was experimental data; days 1 to 24 and then days 37 and 44. This meant that the evaluation on these variables simply omitted the model performance between days 25 and 36 since there was no experimental data with which to compare. Consequently, the reduced number of days on which to validate the models, resulted in a higher critical F value in the F-test method of hypothesis testing and lead to a conclusion that the difference in alkalinity prediction between the models was not significant at a 95% confidence level. This was disappointing in that AD-FTRW2 presented a marked improvement (~12%) on alkalinity prediction.

5.2.3 *Influence of carbon dioxide expulsion/dissolution kinetics*

In looking at the results of the comparative model performance, it was noted that pH and alkalinity predictions were strongly affected by the kinetics of carbon dioxide expulsion/dissolution. Following an investigation on the effect of adapting the carbon dioxide expulsion/dissolution kinetics on pH, it was clear that AD-FTRW2 was far more sensitive to adjustments in the CO_2 expulsion/dissolution kinetics. This was regarded as a good sign for the revised model (AD-FTRW2) since there is a strong interaction between this process and reactor pH considering that the carbonate system is the dominant weak acid base system in FTRW.

In comparing the performance of AD-FTRW1 versus AD-FTRW2 on reactor pH, it can be seen that both models exhibit similar profiles except AD-FTRW1 is vertically shifted by approximately 0.3 pH units. The physico-chemical model for AD-FTRW1 was developed to be valid for a pH range of 6.5 to 7.5 while the physico-chemical model for AD-FTRW2 was developed to be valid for a pH range of 3.5 to 9. Since the data set was within the validity ranges of both models underlying physico-chemical formulations (the operational pH range for this dataset was between 7 and 7.5), the similar profiles could be expected. It is noted that it would be interesting to simulate an experimental dataset where reactor pH falls outside of the range of 6.5 to 7.5 and then compare the performances of AD-FTRW1 and AD-FTRW2. In line with this the modelling of reactor failure should also be investigated.

5.2.4 *Influence of increasing organic load on model predictions*

Another observation on the performance of each model for pH prediction, is that AD-FTRW2 performed best from day 1 to 28 and thereafter AD-FTRW1 performed better. The latter period corresponds to the time when the organic loading rate to the reactor begins to increase sharply. If however one looks at the derivatives of pH with respect to time for both models at day 44, it can be seen that AD-FTRW2 interestingly exhibits signs of recovering towards the experimental data. It is speculated that perhaps there is an imbalance on the biological side of both models whereby processes that are responsible for liquor souring (acetogenic processes) are responding faster to the increase in organic loading rate than those processes responsible for liquor sweetening (methanogenic processes). This should be investigated further.

5.3 Kinetic vs. ionic differences between models

When one looks at the comparative modelling results for AD-FTRW1 and AD-FTRW2, it is interesting to note that that not much improvement was achieved on biologically dependant variables as compared to the physico-chemically dependent variables. Effluent SCFA concentration (a surrogate for effluent COD) and mixed liquor suspended solids are identified as process variables that are solely dependent on the biological side of the models while reactor pH, alkalinity and biogas production are influenced to a large extent by the physico-chemical side of the models (although the biological interaction with these process variables cannot be discounted). For pH and alkalinity this distinction is quite clear but for biogas its classification as a physico-chemically dependent variable needs some explanation. Biogas is most significantly made up of carbon dioxide and methane. Both of these components are derived from the bioprocesses however carbon dioxide, according to the model formulation, is synthesized in the form of carbonic acid. This then enters the ionic speciation sub-routine and according to that redistribution is evolved via the carbon dioxide expulsion/dissolution process. It is therefore clear that biogas production whilst also dependent on the biological side of the model, is significantly influenced by the physico-chemical modelling. The fact that the results show significant improvement (AD-FTRW1 vs AD-FTRW2) on the physico-chemically dependent process variables and then similar profiles for the biologically dependent process variables gives testament to the model development philosophy that only

the physico-chemical modelling in AD-FTRW1 was adapted in AD-FTRW2 and that all biological modelling was left unchanged.

Another concern raised by the model evaluation results is that both AD-FTRW2 and AD-FTRW1 systematically under-predict all the process variables relevant to the mass balance of the system; these variables include biogas production, effluent SCFA concentration and mixed liquor suspended solids. This points to either a fundamental problem in mass conservation laws applied during model development or towards inaccurate experimental data. Mass conservation within the model was verified during a comprehensive atomic balancing procedure and it is therefore suspected that there are some errors on the side of the experimental data. According to Van Zyl (2005), the biogas experimental data set was thought to be the least reliable due to instrumentation challenges that the experimental work faced. This together with the fact that the model validation procedure only had access to this limited data set implies that AD-FTRW2 needs to undergo further validation on newly generated experimental data. This is noted as a recommendation for future research.

6 CONCLUSION

This research undertook to develop and improve Sasol Technology's existing anaerobic digestion model (AD-FTRW1) through enhanced physico-chemical modelling and with special focus on the accuracy of its pH predictions. This was identified as an important engineering development to assist in advanced process control of anaerobic digestors treating such effluents. Physico-chemical modelling was to be enhanced through the incorporation of a dedicated ionic speciation sub-routine and through the refinement of carbon dioxide expulsion/dissolution kinetics. The hypothesis of the study was that:

The pH prediction in AD-FTRW1 will be improved through the incorporation of a more comprehensive ionic speciation model.

The results of this dissertation support the research hypothesis.

In addition, the following significant outcomes and conclusions were reached:

1) AD-FTRW2 has been successfully developed to include a comprehensive ionic speciation sub-routine and enhanced gas exchange modelling.
2) AD-FTRW2 also includes developments in the form of phosphorous uptake representation and a parameterized biomass formula.
3) A process and preliminary criteria were developed for ionic species inclusion in a system tailored ionic speciation sub-routine.
4) Comparative model performance revealed that AD-FTRW2 performed better than AD-FTRW1 in simulating the given data set for all variables except effluent SCFA concentration.
5) Statistical analysis revealed that the only variable that was predicted significantly better in AD-FTRW2 was pH.
6) It is concluded that further model validation is required to determine whether AD-FTRW2 predicts significantly more accurately than AD-FTRW1 on all the process variables. For this further dynamic experimental data is required.
7) The inclusion of the ionic speciation sub-routine has resulted in a reduced simulation speed in AD-FTRW2.

7 RECOMMENDATIONS

This study has completely achieved its original objectives; however the following general recommendations are presented for future research on this topic.

1. The feed equilibration calculation should be integrated into the WEST configuration for further research using the data or experimental procedure adopted in this study and in Van Zyl (2008).
2. At this point it should be stated that the modelling of process inhibitions in the AD-FTRW environment merits an extensive experimental study.
3. It is noted that it would be interesting to simulate an experimental dataset where reactor pH falls outside of the range of 6.5 to 7.5 and then compare the performances of AD-FTRW1 and AD-FTRW2 since the ionic speciation approach of AD-FTRW2 is theoretically capable of predicting pH from aqueous phase equilibria in a much wider range then the integrated approach of AD-FTRW1.
4. AD-FTRW2 needs to undergo further validation on newly generated experimental data in order to test its more general applicability and also to determine whether the improved predictive capacity displayed in the variables (biogas production, alkalinity) other than pH are also significant.

REFERENCES

Batstone, D. J., Keller, J., Angelidaki, I., Kalyuzhnyi, S. V., Pavlostathis, S. G., Rozzi, A., ... & Vavilin, V. A. (2002). The IWA Anaerobic Digestion Model No 1(ADM 1). Water Science & Technology, 45(10), 65-73.

Batstone, D. J., Amerlinck, Y., Ekama, G., Goel, R., Grau, P., Johnson, B., ... & Volcke, E. (2012). Towards a generalized physicochemical framework. Water Science and Technology, 66(6), 1147.

Brouckaert, C. J., D. Ikumi, et al. (2010). "A 3-phase anaerobic digestion model." To be submitted.

Davies, O. L. (1947). Statistical methods in research and production. Statistical methods in research and production.

Dochain, D., & Vanrolleghem, P. (2001). Dynamical modelling and estimation in wastewater treatment processes. International Water Assn.

Dold, P. L., Ekama, G. A., & Marais, G. (1980). A general model for the activated sludge process. Progress in Water Technology, 12(6).

Dyson, F. (2004). A meeting with Enrico Fermi. Nature, 427(6972), 297-297.

Ekama, G. A. (2009). Using bioprocess stoichiometry to build a plant-wide mass balance based steady-state WWTP model. Water research, 43(8), 2101-2120.

Gross, D. (2006). Thanks for cheap gas, Mr. Hitler!. SLATE, October, 23, 2006.

Hall-Green, M. (2000). Sasol, 50 years of innovation. Corporate Communications Department. S. P. Ltd. Johannesburg, Ultra Litho.

Hauduc, H., Neumann M. (2011). Towards quantitative quality criteria to evaluate simulation results in wastewater treatment - A critical review. 8th International IWA Symposium on Systems Analysis and Integrated Assessment in Water Management (WATERMATEX2011), San Sebastian, Spain.

Henze, M. (2008). Biological Wastewater Treatment: Principles, Modeling, and Design. International Water Assn. London

Jeppsson, U., Pons, M. N., Nopens, I., Alex, J., Copp, J. B., Gernaey, K. V., ... & Vanrolleghem, P. A. (2007). Benchmark simulation model no 2: general protocol and exploratory case studies. Water Science and Technology, 56(8), 67-78.

Kalyuzhnyi, S. V., Martinez, E. P., & Martinez, J. R. (1997). Anaerobic treatment of high-strength cheese-whey wastewaters in laboratory and pilot UASB-reactors. Bioresource Technology, 60(1), 59-65.

Kops, S., Vangheluwe, H., Claeys, F., Vanrolleghem, P., Yuan, Z., & Vansteenkiste, G. (1999). The process of model building and simulation of ill-defined systems: Application to wastewater treatment. Mathematical and Computer Modelling of Dynamical Systems, 5(4), 298-312.

Legates, D. R., & McCabe, G. J. (1999). Evaluating the use of “goodness-of-fit” measures in hydrologic and hydroclimatic model validation. Water Resources Research, 35(1), 233-241.

Loewenthal, R. E., Ekama, G. A., & Marais, G. (1989). Mixed weak acid/base systems. Part 1- Mixture characterisation. Water S. A., 15(1), 3-24.

McCarty, P. L. (1972). Stoichiometry of biological reactions. Paper presented at the international conference, Toward a unified concept of biological waste treatment design Atlanta, 6 October 1972.

Musvoto, E. V., Wentzel, M. C., Loewenthal, R. E., & Ekama, G. A. (1997). Kinetic-based model for mixed weak acid/base systems. WATER SA-PRETORIA, 23, 311-322.

Olsson, G., & Newell, R. B. (1999). Wastewater treatment systems: modelling, diagnosis and control. International Water Assn.

Phillips, T. D. & du Toit, F. J. (2002). Water Reuse and Recycling at Sasol. 3rd International Conference & Exhibition on Integrated Environmental Management in Southern Africa. Johannesburg, South Africa.

Rosen, C., Vrecko, D., Gernaey, K. V., & Jeppsson, U. (2005). Implementing ADM1 for benchmark simulations in Matlab/Simulink. In Proceedings of the First International Workshop on the IWA Anaerobic Digestion Model No. 1 (pp. 4-6). September, 2005, Copenhagen, Denmark

Schunn, C.D., and Wallach, D. (2005). Evaluating goodness-of-fit in comparison of models to data. In W. Tack (Ed.), Psychologie der Kognition: Reden and Vorträge anlässlich der Emeritierung von Werner Tack (pp. 115-154). Saarbrueken, Germany, University of Saarland Press

Sötemann, S. W., Van Rensburg, P., Ristow, N. E., Wentzel, M. C., Loewenthal, R. E., & Ekama, G. A. (2006). Integrated chemical/physical and biological processes

modeling Part 2 - Anaerobic digestion of sewage sludges.Water SA, 31(4), 545-568.

Stumm, W., & Morgan, J. J. (1995). Aquatic chemistry: chemical equilibria and rates in natural waters. JOHN WILEY & SONS, NEW YORK, NY 10158(USA). 1995.

Van Griensven, A., Francos, A., & Bauwens, W. (2002). Sensitivity analysis and auto-calibration of an integral dynamic model for river water quality. Water Science and Technology, 325-332.

van Zyl, P. J. (2008). Anaerobic Digestion of Fischer Tropsch Reaction Water; Submerged Membrane Anaerobic Reactor Design, Performance Evaluation and Modeling. Civil Engineering, Cape Town, UCT. Phd: 259.

Vanhooren, H., Meirlaen, J., Amerlinck, Y., Claeys, F., Vangheluwe, H., & Vanrolleghem, P. (2003). WEST: modelling biological wastewater treatment.Journal of Hydroinformatics, 5, 27-50.

APPENDIX

7.1 Derivation and Reconciliation of AD-FTRW1's Acetoclastic Methanogenesis Stochiometry

Required to Prove:

A case study on Acetoclastic Methanogenesis was undertaken in order to fully understand what speciation chemistry had been integrated into ADFTrev24's model stoichiometry and how the final stoichiometric equations were arrived at. The importance of this exercise is to understand the mechanics of the previous model, so as to be able to highlight the differences between it and the new modelling approach.

1) Acetoclastic Methanogenesis Stoichiometry according to ADFTrev2 and P. Van Zyl's Thesis along with relevant model assumptions.

According to some case-limiting assumptions, Acetoclastic Methanogenesis is implemented in the format laid out below in ADFTrev24.

$$\frac{5}{2Y_{am}}C_2H_4O_2 + NH_4^+ + \frac{(5-11Y_{am})}{2Y_{am}}H_2O \rightarrow \frac{(5-3Y_{am}-5F_{am})}{2Y_{am}}H_2CO_3 + \frac{(5F_{am}-2Y_{am})}{2Y_{am}}HCO_3^- + C_5H_7O_2N + \frac{(5-5Y_{am})}{2Y_{am}}CH_4 \quad \text{Eq(A)}$$

The stoichiometry of Acetoclastic Methanogenesis as it appears in the body of P. Van Zyl's thesis (page 155).

$$\frac{5(1-F_{am})}{2Y_{am}}C_2H_4O_2 + \frac{5F_{am}}{2Y_{am}}C_2H_3O_2^- + NH_4^+ + \frac{(5-11Y_{am})}{2Y_{am}}H_2O + \frac{(5-3Y_{am}-5F_{am})}{2Y_{am}}H_2CO_3 \rightarrow \frac{(5-2Y_{am})}{2Y_{am}}HCO_3^- + C_5H_7O_2N + \frac{(5-5Y_{am})}{2Y_{am}}CH_4 \quad \text{Eq(B)}$$

Important model assumptions:

1. All CO_2 produced will be in the soluble form of H_2CO_3: $CO_2 + H_2O \rightarrow H_2CO_3$
2. The carbonate system acts as the proton source/sink for all weak acid base chemistry reactions.
3. The contribution of CO_3^{2-} is regarded as negligible in the anaerobic digestion pH range.
4. Only the protonated (non-ionic) form of any SCFA can be metabolized.
5. An un-protonated (ionic) SCFA must 1st pick up a proton from the carbonate system prior to its metabolism: $C_xH_{y-1}O_z^- + H_2CO_3 \rightarrow C_xH_yO_z + HCO_3^-$
6. The degree to which influent SCFA's dissociate is determined by the influent pH and is implemented via the F value: $F_{Cx} = \frac{C_xH_{y-1}O_z^-}{(C_xH_{y-1}O_z + C_xH_yO_z)} = \frac{1}{\left(1+\frac{[H^+]_{feed}}{K_{ax}}\right)}$
7. Saline ammonia (NH_4^+) needs to be deprotonated before it can be used by the FOGs: $NH_4^+ + HCO_3^- \rightarrow NH_3 + H_2CO_3$

Proof:

The proof involves a 1st principles approach to the derivation based on the AD stoichiometric theory presented in (Ekama 2009) in an attempt to arrive at the final expressions implemented in ADFTrev24.

1) Generalized Catabolic Equation for Anaerobic Digestion (Ekama 2009)

$$C_xH_yO_zN_aP_b + (2x - z + a + 3b)H_2O \xrightarrow{Catabol.} (x - a + b)CO_2 + aNH_4^+ + bH_2PO_4^- + (a - b)HCO_3^- + \gamma_s[H^+ + e^-]$$

Where $\gamma_s = 4x + y - 2z - 3a + 5b$ and is referred to as the Electron-Donating capacity of the substrate.

2) For Acetic Acid with a molecular formula of: $CH_3COOH \Rightarrow C_2H_4O_2 \quad x = 2 \quad y = 4 \quad z = 2 \quad a = 0 \quad and \quad b = 0$

Direct substitution of the above constants into the generalized AD catabolic expression yields the following equation for the catabolism of Acetic Acid:

$$C_2H_4O_2 + 2H_2O \xrightarrow{Catabolism\ of\ Acetic\ Acid} 2CO_2 + 8[H^+ + e^-]$$ .....Eq(C)

With $\gamma_S = 8$.

3) Generalized Anabolic Equation for Anaerobic Digestion (Ekama 2009)

$$(k - n + p)CO_2 + nNH_4^+ + pH_2PO_4^- + (n - p)HCO_3^- + \gamma_B[H^+ + e^-] \rightarrow C_kH_lO_mN_nP_p + (2k - m + n + 3p)H_2O$$

Where $\gamma_B = 4k + l - 2m - 3n + 5p$ and is referred to as the electron-accepting capacity of the biomass.

4) In P. Van Zyl's study, the biomass is represented as: $C_5H_7O_2N \Rightarrow k = 5 \quad l = 7 \quad m = 2 \quad n = 1 \quad and \quad p = 0$

Direct substitution of the above constants into the generalized AD anabolic expression yields the following equation for the anabolism of biomass:

$$4CO_2 + NH_4^+ + HCO_3^- + 20[H^+ + e^-] \rightarrow C_5H_7O_2N + 9H_2O$$
.....Eq(D)

With $\gamma_B = 20$

5) In AD, carbon dioxide acts as the terminal electron acceptor; reducing to methane according to the following chemical equation.

$$8[H^+ + e^-] + CO_2 \rightarrow CH_4 + 2H_2O$$ .....Eq(E)

6) Equation C-E can then be combined in the following ratios in order to yield the overall metabolic reaction for Acetoclastic Methanogenesis.

$$Eq(C) + Y_{am}\frac{\gamma_S}{\gamma_B}Eq(D) + (1 - Y_{am})\frac{\gamma_S}{8}Eq(E) = 0$$

This yields: $\boxed{C_2H_4O_2 + \frac{2Y_{am}}{5}NH_4^+ + \frac{2Y_{am}}{5}HCO_3^- \rightarrow \frac{8Y_{am}}{5}H_2O + \left(\frac{5-3Y_{am}}{5}\right)CO_2 + \frac{2Y_{am}}{5}C_5H_7O_2N + (1 - Y_{am})CH_4}$.....Eq(F)

The above equation for the Anaerobic Metabolism of Acetoclastic Methanogenesis follows directly the methodology outlined in the paper by (Ekama 2009). In order to reconcile this (Eqn(F)) stoichiometry with Eqn(A) and Eqn(B), the relevant model assumptions and speciation chemistry needs to be integrated into the stoichiometry together with some fundamental algebraic manipulations.

7) Reconciliation of Eqn(F) with Eqn(A) and Eqn(B)

1st multiply Eqn(F) by $\frac{5}{2Y_{am}}$ which gives:

$$\frac{5}{2Y_{am}}C_2H_4O_2 + NH_4^+ + HCO_3^- \rightarrow 4H_2O + \left(\frac{5-3Y_{am}}{2Y_{am}}\right)CO_2 + C_5H_7O_2N + \left(\frac{5-5Y_{am}}{2Y_{am}}\right)CH_4 \quad \text{Eq(F1)}$$

According to assumption 1 on the previous page, re-express all CO2 produced in its soluble form, by combining it with some of the H2O produced to form carbonic acid. This action yields;

$$\frac{5}{2Y_{am}}C_2H_4O_2 + NH_4^+ + HCO_3^- \rightarrow \left(\frac{11Y_{am}-5}{2Y_{am}}\right)H_2O + \left(\frac{5-3Y_{am}}{2Y_{am}}\right)H_2CO_3 + C_5H_7O_2N + \left(\frac{5-5Y_{am}}{2Y_{am}}\right)CH_4 \quad \text{Eq(F2)}$$

What has not yet been incorporated into the stoichiometry is the speciation of the influent SCFA's. As has been mentioned previously, the degree to which the SCFA's dissociate is pH dependent and incorporated as a parameter in the stoichiometry via an SCFA specific F value; the calculation for which is depicted above. In terms of F, Acetic acid speciates according to the following equation:

$$C_2H_4O_2 \rightarrow (1-F)C_2H_4O_2 + FC_2H_3O_2^- + FH^+ \quad \text{Eq(F3)}$$

Multiplying Eq(F3) by $\frac{5}{2Y_{am}}$ yields:

$$\frac{5}{2Y_{am}}C_2H_4O_2 \rightarrow \frac{5-5F}{2Y_{am}}C_2H_4O_2 + \frac{5F}{2Y_{am}}C_2H_3O_2^- + \frac{5F}{2Y_{am}}H^+ \quad \text{Eq(F4)}$$

Eq(F4) is then substituted directly into Eq(F2) with HCO_3^- treated as the proton sink and this (after some simple algebraic manipulations) yields the final model equation for Acetoclastic Methanogenesis.

$$\boxed{\frac{5(1-F)}{2Y_{am}}C_2H_4O_2 + \frac{5F}{2Y_{am}}C_2H_3O_2^- + NH_4^+ + \frac{(5-11Y_{am})}{2Y_{am}}H_2O + \frac{(5F+3Y_{am}-5)}{2Y_{am}}H_2CO_3 \rightarrow \frac{(5F-2Y_{am})}{2Y_{am}}HCO_3^- + C_5H_7O_2N + \frac{(5-5Y_{am})}{2Y_{am}}CH_4} \quad \text{Eq(G)}$$

Discussion

Acetoclastic Methanogenesis Stoichiometry as it appears in ADFTrev24

$$\frac{5}{2Y_{am}}C_2H_4O_2 + NH_4^+ + \frac{(5-11Y_{am})}{2Y_{am}}H_2O \rightarrow \frac{(5-3Y_{am}-5F_{am})}{2Y_{am}}H_2CO_3 + \frac{(5F_{am}-2Y_{am})}{2Y_{am}}HCO_3^- + C_5H_7O_2N + \frac{(5-5Y_{am})}{2Y_{am}}CH_4$$

.....Eq(A)

Acetoclastic Methanogenesis Stoichiometry as it appears in the body of P. Van Zyl's thesis

$$\frac{5(1-F_{am})}{2Y_{am}}C_2H_4O_2 + \frac{5F_{am}}{2Y_{am}}C_2H_3O_2^- + NH_4^+ + \frac{(5-11Y_{am})}{2Y_{am}}H_2O + \frac{(5-3Y_{am}-5F_{am})}{2Y_{am}}H_2CO_3 \rightarrow \frac{(5-2Y_{am})}{2Y_{am}}HCO_3^- + C_5H_7O_2N + \frac{(5-5Y_{am})}{2Y_{am}}CH_4$$

.....Eq(B)

Acetoclastic Methanogenesis Stoichiometry according to C.Lees derivation

$$\frac{5(1-F)}{2Y_{am}}C_2H_4O_2 + \frac{5F}{2Y_{am}}C_2H_3O_2^- + NH_4^+ + \frac{(5-11Y_{am})}{2Y_{am}}H_2O + \frac{(5F+3Y_{am}-5)}{2Y_{am}}H_2CO_3 \rightarrow \frac{(5F-2Y_{am})}{2Y_{am}}HCO_3^- + C_5H_7O_2N + \frac{(5-5Y_{am})}{2Y_{am}}CH_4$$

.....Eq(G)

**Expressions which differ from equation to equation are in red. Otherwise the stoichiometry corresponds exactly.*

7.2 Generalized Biological Process Stoichiometry Derivation

7.2.1 *Acidogenesis*

NA

7.2.2 *Acetogenesis*

Source is P. Van Zyl and Brouckaert

In deriving the stoichiometry for acetogenesis, the method outlined by Van Zyl was followed; this is an adaptation of the method outlined by Ekama.

1) Catabolism
    a. Generalized Catabolic Equation for Short Chain Fatty Acids of general formula $C_xH_{2x}O_2$ where x > 3

$$C_xH_{2x}O_2 + 2H_2O \rightarrow C_2H_4O_2 + C_{x-2}H_{2(x-2)}O_2 + 2H_2 \quad For\ x > 3$$

If we adapt this equation for the full dissociation of SCFA's (a modelling necessity) the above equation yields.

$$C_xH_{2x-1}O_2^- + 2H_2O \rightarrow C_2H_3O_2^- + C_{x-2}H_{2(x-2)-1}O_2^- + H^+ + 2H_2 \quad For\ x > 3$$

b. Catabolic Equation for the Acetogenesis of Propanoic Acid

$$C_3H_6O_2 + 2H_2O \rightarrow C_2H_4O_2 + CO_2 + 3H_2$$

$$but\ CO_2 = 2H^+ + CO_3^{2-} - H_2O$$

If we adapt this equation for the full dissociation of SCFA's (a modelling necessity) and apply the abovementioned identity the above equation yields.

$$C_3H_5O_2^- + 3H_2O \rightarrow C_2H_3O_2^- + CO_3^{2-} + 2H^+ + 3H_2$$

c. Catabolic Equation for the Acetogenesis of Ethanol

$$C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 2H_2$$

If we adapt this equation for the full dissociation of SCFA's (a modelling necessity) the above equation yields.

$$C_2H_6O + H_2O \rightarrow C_2H_3O_2^- + H^+ + 2H_2$$

2) Generalized Anabolic Equation used for Acetogenic processes

$$C_xH_yO_zN_aP_b \rightarrow \frac{\gamma_s}{\gamma_B}C_kH_lO_mN_nP_p + \left(3b + 2x - a + (n - 3p - 2k)\frac{\gamma_s}{\gamma_B}\right)H^+ + \left(z - 3x - 4b + (3k - m + 4p)\frac{\gamma_s}{\gamma_B}\right)H_2O + \left(x - \frac{\gamma_s}{\gamma_B}k\right)CO_3^{2-} + \left(a - \frac{\gamma_s}{\gamma_B}n\right)NH_4^+ + \left(b - \frac{\gamma_s}{\gamma_B}p\right)PO_4^{3-}$$

3) Generalized Overall Metabolic Equation for Acetogenesis

This is created by combining the anabolic and catabolic reactions in the following ratio related to the biomass yield per substrate:

$$Metabolic = Y \times Anabolic + (1 - Y) \times Catabolic$$

Due to the variability of the acetogenic catabolic processes, an overall generalized metabolic equation for acetogenesis of any substrate into any organism is not represented here. It would be complex and unnecessary.

7.2.3 *Methanogenesis*

Source is Ekama

In deriving the stoichiometry for methanogenesis, the method outlined by Ekama was followed.

8) Generalized Catabolic Equation for Anaerobic Digestion (Ekama 2009)

Relevant to Methanogenesis only

$$C_xH_yO_zN_aP_b + (2x - z + a + 3b)H_2O \xrightarrow{Catabol.} (x - a + b)CO_2 + aNH_4^+ + bH_2PO_4^- + (a - b)HCO_3^- + \gamma_s[H^+ + e^-]$$

Where $\gamma_s = 4x + y - 2z - 3a + 5b$ and is referred to as the Electron-Donating capacity of the substrate.

9) Generalized Anabolic Equation for Anaerobic Digestion (Ekama 2009)

Relevant to Methanogenesis only

$$(k - n + p)CO_2 + nNH_4^+ + pH_2PO_4^- + (n - p)HCO_3^- + \gamma_B[H^+ + e^-] \rightarrow C_kH_lO_mN_nP_p + (2k - m + n + 3p)H_2O$$

Where $\gamma_B = 4k + l - 2m - 3n + 5p$ and is referred to as the electron-accepting capacity of the biomass.

10) In AD, carbon dioxide acts as the terminal electron acceptor; reducing to methane according to the following chemical equation.

$$8[H^+ + e^-] + CO_2 \rightarrow CH_4 + 2H_2O$$ .....Eq(E)

11) Equation A – C can then be combined in the following ratios in order to yield the overall metabolic reaction for Acetoclastic Methanogenesis.

$$Eq(A) + Y_{am}\frac{\gamma_S}{\gamma_B}Eq(B) + (1 - Y_{am})\frac{\gamma_S}{8}Eq(C) = 0$$

12) Generalized Overall Metabolic Equation for Anaerobic Digestion.

Relevant to Methanogenesis only. Or overall AD process from feed subtrates to end of line products.

$$C_xH_yO_zN_aP_b + \left(2x - z + a + 3b - Y\frac{\gamma_S}{\gamma_B}(2k - m + n + 3p) - \frac{2\gamma_S}{8}(1 - Y)\right)H_2O \rightarrow \left(x - a + b - Y\frac{\gamma_S}{\gamma_B}(k - n + p) - \frac{(1-Y)\gamma_S}{8}\right)CO_2 + \left(\frac{\gamma_S}{8}(1 - Y)\right)CH_4 + \left(Y\frac{\gamma_S}{\gamma_B}\right)C_kH_lO_mN_nP_p + \left(a - nY\frac{\gamma_S}{\gamma_B}\right)NH_4^+ + \left(b - pY\frac{\gamma_S}{\gamma_B}\right)H_2PO_4^- + \left(a - b - Y\frac{\gamma_S}{\gamma_B}(n - p)\right)HCO_3^-$$

Some reaction components are transformed into speciates of the form in which they are applied/fed in/to the speciation model. The transformations are achieved via the following identities:

$$CO_2 = 2H^+ + CO_3^{2-} - H_2O$$

$$H_2PO_4^- = 2H^+ + PO_4^{3-}$$

$$HCO_3^- = H^+ + CO_3^{2-}$$

Direct substitution of the above identities yields the following overall equation for methanogenesis in terms of the speciation model read components:

$$C_xH_yO_zN_aP_b + \left(3x - z + 4b - Y\frac{\gamma_s}{\gamma_B}(3k - m + 4p) - \frac{3\gamma_s}{8}(1 - Y)\right)H_2O$$
$$\rightarrow \left(x - Y\frac{\gamma_s}{\gamma_B}(k) - \frac{(1 - Y)\gamma_s}{8}\right)CO_3^{2-}$$
$$+ \left(2x - a + 3b - Y\frac{\gamma_s}{\gamma_B}(2k - n + 3p) - \frac{2\gamma_s}{8}(1 - Y)\right)H^+ + \left(\frac{\gamma_s}{8}(1 - Y)\right)CH_4$$
$$+ \left(Y\frac{\gamma_s}{\gamma_B}\right)C_kH_lO_mN_nP_p + \left(a - nY\frac{\gamma_s}{\gamma_B}\right)NH_4^+ + \left(b - pY\frac{\gamma_s}{\gamma_B}\right)PO_4^{3-}$$

7.3 Matlab Bioprocess Stoichiometry Generators

7.3.1 *Acidogenesis*

```
% Hydrolysis and Acidogenesis
% EBIOMASS is endogenous biomass
%Initialize symbols
syms x y z a b Y Gs Gb k l m n p
syms SUBSTRATE EBIOMASS BIOMASS H H2O CO3 NH4 NH3 PO4 Eqn1 Eqn2
syms  parameters_l parameters_m parameters_n parameters_p parameters_Y
syms  parameters_Gb CH4 Ac

%Set up stoichiometry of reaction components
%Substrate CxHyOzNaPb
%Specify x,y,z,a,b
x = 2;
y = 4;
z = 2;
a = 0 ;
```

```
b = 0 ;

Gs = 4*x+y-2*z-3*a+5*b

SUBSTRATE = Ac + H

%Biomass C(k)H(l)O(m)N(n)P(p)

k = 1 ;

l = parameters_l ;

m = parameters_m ;

n = parameters_n ;

p = parameters_p ;

% Gb = 4*k+l-2*m-3*n+5*p

% Commented out because it is neater to have Gb as a parameter in WEST
to

% facilitate a variable biomass formula for increased model
versatility.

Gb = parameters_Gb ;

Eqn1  = + SUBSTRATE ...

               - (Gs/Gb)*EBIOMASS ...

               - (3*b+2*x-a+(n-3*p-2*k)*Gs/Gb)*H ...

               - (z-3*x-4*b+(3*k-m+4*p)*Gs/Gb)*H2O ...

               - (x-Gs/Gb*k)*CO3 ...

               - (a-Gs/Gb*n)* NH4 ...

               - (b-Gs/Gb*p)* PO4


Eqn2 = -EBIOMASS + BIOMASS


Final = parameters_Y*Eqn2 + (1-parameters_Y)*(Gb/Gs)*Eqn1


ProductCoeff = collect(Final,[BIOMASS EBIOMASS Ac H2O H CO3 NH4 PO4])
```

7.3.2 *Acetogenesis*

```
%Script to generate stoichiometric coefficients for Acetogenesis of
...

%Hexanoic Acid, Valeric Acid, Butyric Acid, Propionic Acid + Ethanol
ONLY.
```

```
%-------------------------------------------------------------------------

clear all

%Initialize variables

s = 0

d = 0

r = 0

%Initialize symbols

syms x y z a b Y Gs Gb k l m n p

syms SUBSTRATE BIOMASS REM H H2O CO3 NH4 NH3 PO4 anabolic catabolic

syms Hex Val But Prop Ac Eth H2

syms  parameters_l parameters_m parameters_n parameters_p parameters_Y

syms  parameters_Gb CH4 Ac


%Set up stoichiometry of reaction components

%Substrate CxHyOzNaPb

%It is only necessary to specify the x parameter as either 6,5,4,3 or
2

x = 4                    %specify x as 6,5,4,3,2 ----only necessary
specification

a = 0 ;          %Catabolic general equation does not accomodate N and
P

b = 0 ;          %Catabolic general equation does not accomodate N and
P


%Biomass C(k)H(l)O(m)N(n)P(p)

k = 1 ;

l = parameters_l ;

m = parameters_m ;

n = parameters_n ;

p = parameters_p ;

% Gb = 4*k+l-2*m-3*n+5*p

% Commented out because it is neater to have Gb as a parameter in WEST
to

% facilitate a variable biomass formula for increased model
versatility.
```

```
Gb = parameters_Gb ;
if x == 6
    SUBSTRATE = Hex + H
    REM = But + H ;
    y = 12 ;
    z = 2 ;
    d = 1 ;
    r = 2 ;
    s = 2 ;
elseif x == 5
    SUBSTRATE = Val + H
    REM = Prop + H ;
    y = 10 ;
    z = 2 ;
    d = 1 ;
    r = 2 ;
    s = 2 ;
elseif x == 4
    SUBSTRATE = But + H
    REM = Ac + H ;
    y = 8 ;
    z = 2 ;
    d = 1 ;
    r = 2 ;
    s = 2 ;
elseif x == 3
    SUBSTRATE = Prop + H
    REM = CO3 + 2*H - H2O ;
    y = 6 ;
    z = 2 ;
    d = 1 ;
    r = 3 ;
```

```
    s = 2 ;
elseif x == 2
    SUBSTRATE = Eth
    REM = 0 ;
    y = 6 ;
    z = 1 ;
    d = 0 ;
    r = 2 ;
    s = 1 ;
else disp('x parameter is outside the scope of this script')
end
Gs = 4*x+y-2*z -3*a+5*b
% if statement to run the equation generator or not
if x == 6 || 5 || 4 || 3 || 2

    anabolic = - SUBSTRATE ...
               + (Gs/Gb)*BIOMASS ...
               + (3*b+2*x-a+(n-3*p-2*k)*Gs/Gb)*H ...
               + (z-3*x-4*b+(3*k-m+4*p)*Gs/Gb)*H2O ...
               + (x-Gs/Gb*k)*CO3 ...
               + (a-Gs/Gb*n)* NH4 ...
               + (b-Gs/Gb*p)* PO4

    catabolic = - SUBSTRATE ...
                - s*H2O ...
                + Ac + H ...
                + d*REM ...
                + r*H2
    final = parameters_Y*anabolic + (1-parameters_Y)*catabolic
    % collect stoichiometric coefficients for Petersen matrix
    ProductCoeff = collect(final,[BIOMASS Hex Val But Prop Eth Ac H2O
H CO3 NH4 PO4])
```

```
else break

end
```

7.3.3 *Methanogenesis*

```
clear all

%_____________________________________

% This file is useful for methanogenic processes only ie acetoclastic,
hydrogenotrophic

% and methanol methanogenesis.

% The file is easily manipulated to suit the various substrates
through modification

% of the substrates chemical formula via the x,y,z,a,b parameters.

%                              WEST                                paprameters:
      parameters_Y,parameters_Gb,parameters_l,parameters_m,parameteres
_n

%                  parameters_p

% declare symbolic variables

syms x y z a b Gs Gb k l m n p HAc CO2 HCO3

syms REAGENT BIOMASS H H2O CO3 NH4 NH3 PO4 anabolic catabolic

syms parameters_l parameters_m parameters_n parameters_p parameters_Y

syms parameters_Gb CH4 H2 Meth HAc Y SUBSTRATE

%_____________________________________

% set up stoichiometry of reaction components

% stoichiometric numbers:

% x,k for C; y,l for H; z,m for O; a,b for N; b,p for P; Gs,Gb for
redox electrons

%_____________________________________

% REAGENT : (CxHyOzNaPb) ---> Manipulate x,y,z,a,b to suit

% the substrate

% H2 ---> x = 0; y = 2; z = 0; a = 0; b = 0

% Meth -> x = 1; y = 4; z = 1; a = 0; b = 0

% H+Ac ---> x = 2; y = 4; z = 2; a = 0; b = 0

x = 2 ; y = 4 ; z = 2 ; a=0 ; b=0 ; Gs=4*x+y-2*z-3*a+5*b ;
```

```
if x == 0

    SUBSTRATE = H2

else if x == 1

        SUBSTRATE = Meth

    else SUBSTRATE = HAc

    end

end

% BIOMASS = C(k)H(l)O(m)N(n)P(p) (biomass)

k = 5 ; l = 7 ; m = 2 ; n=1 ; p=0 ;

% the underscores in the parameters above are changed to dots when
cutting

% and pasting the results to WEST.

Gb=4*k+l-2*m-3*n+5*p ;

% commented out because it is more versatile to have Gb as a
calculated parameter in WEST

% Gb = parameters_Gb ;

%_____________________________________

% reaction stoichiometry in the form (products - reactants)

final = - SUBSTRATE ...

      -(2*x-z+a+3*b-Y*(Gs/Gb)*(2*k-m+n+3*p)-2*(Gs/8)*(1-Y))*H2O ...

      +(Y*(Gs/Gb))*BIOMASS ...

      +((Gs/8)*(1-Y))*CH4 ...

      +(x-a+b-Y*Gs/Gb*(k-n+p)-(1-Y)*Gs/8)*CO2...

      +(a-b-Y*Gs/Gb*(n-p))*HCO3...

      +(a-n*Y*(Gs/Gb))*NH4 ...

      +(b-p*Y*(Gs/Gb))*PO4


%collect stoichiometric co-efficients for Petersen Matrix

ProductCoeff = collect(final,[BIOMASS H2 Meth HAc H2O CO2 HCO3 NH4 PO4
CH4])

%end
```

7.4 Code generated bioprocess stoichiometry

Please note: Each process has its own specific yield coefficients and functional organism groups. It is important to differentiate between the different process parameters with use of subscripts containing process initials.

7.4.1 *Acidogenesis Growth*

```
ProductCoeff =

BIOMASS(Zad) + (-1/parameters_Y)*EBIOMASS(Sbp)
+ (-(parameters_Gb*(parameters_Y - 1))/(8*parameters_Y))*Ac
+     ((parameters_Gb*((32*parameters_p     -     8*parameters_m     +
24)/parameters_Gb - 4)*(parameters_Y - 1))/(8*parameters_Y))*H2O
+     (-(parameters_Gb*((24*parameters_p     -     8*parameters_n     +
16)/parameters_Gb - 3)*(parameters_Y - 1))/(8*parameters_Y))*H
+     (-(parameters_Gb*(8/parameters_Gb     -     2)*(parameters_Y     -
1))/(8*parameters_Y))*CO3
+ (-(parameters_n*(parameters_Y - 1))/parameters_Y)*NH4
+ (-(parameters_p*(parameters_Y - 1))/parameters_Y)*PO4
```

7.4.2 *Hexanoic Acid Acetogenesis Growth*

```
ProductCoeff =

((32*parameters_Y)/parameters_Gb)*BIOMASS - Hex
+ (1 - parameters_Y)*But + (1 - parameters_Y)*Ac
+ (2*parameters_Y + parameters_Y*((128*parameters_p - 32*parameters_m +
96)/parameters_Gb - 16) - 2)*H2O
+ (- parameters_Y - parameters_Y*((96*parameters_p - 32*parameters_n +
64)/parameters_Gb - 11) + 1)*H
+ (-parameters_Y*(32/parameters_Gb - 6))*CO3
+ (-(32*parameters_Y*parameters_n)/parameters_Gb)*NH4
+ (-(32*parameters_Y*parameters_p)/parameters_Gb)*PO4
- 2*H2*(parameters_Y - 1)
```

7.4.3 *Valeric Acid Acetogenesis Growth*

```
ProductCoeff =

((26*parameters_Y)/parameters_Gb)*BIOMASS - Val
+ (1 - parameters_Y)*Prop + (1 - parameters_Y)*Ac
+ (2*parameters_Y + parameters_Y*((104*parameters_p - 26*parameters_m +
78)/parameters_Gb - 13) - 2)*H2O
+ (- parameters_Y - parameters_Y*((78*parameters_p - 26*parameters_n +
52)/parameters_Gb - 9) + 1)*H
+ (-parameters_Y*(26/parameters_Gb - 5))*CO3
+ (-(26*parameters_Y*parameters_n)/parameters_Gb)*NH4
+ (-(26*parameters_Y*parameters_p)/parameters_Gb)*PO4
- 2*H2*(parameters_Y - 1)
```

7.4.4 *Butyric Acid Acetogenesis Growth*

```
ProductCoeff =
```

```
((20*parameters_Y)/parameters_Gb)*BIOMASS - But
+ (2 - 2*parameters_Y)*Ac
+ (2*parameters_Y + parameters_Y*((80*parameters_p - 20*parameters_m +
60)/parameters_Gb - 10) - 2)*H2O
+ (- parameters_Y - parameters_Y*((60*parameters_p - 20*parameters_n +
40)/parameters_Gb - 7) + 1)*H
+ (-parameters_Y*(20/parameters_Gb - 4))*CO3
+ (-(20*parameters_Y*parameters_n)/parameters_Gb)*NH4
+ (-(20*parameters_Y*parameters_p)/parameters_Gb)*PO4
- 2*H2*(parameters_Y - 1)
```

7.4.5 *Propionic Acid Acetogenesis Growth*

```
ProductCoeff =

((14*parameters_Y)/parameters_Gb)*BIOMASS - Prop
+ (1 - parameters_Y)*Ac
+ (3*parameters_Y + parameters_Y*((56*parameters_p - 14*parameters_m +
42)/parameters_Gb - 7) - 3)*H2O
+ (- 2*parameters_Y - parameters_Y*((42*parameters_p - 14*parameters_n
+ 28)/parameters_Gb - 5) + 2)*H
+ (1 - parameters_Y*(14/parameters_Gb - 3) - parameters_Y)*CO3
+ (-(14*parameters_Y*parameters_n)/parameters_Gb)*NH4
+ (-(14*parameters_Y*parameters_p)/parameters_Gb)*PO4
- 3*H2*(parameters_Y - 1)
```

7.4.6 *Ethanol Acetogenesis Growth*

```
ProductCoeff =

((12*parameters_Y)/parameters_Gb)*BIOMASS - Eth
+ (1 - parameters_Y)*Ac
+ (parameters_Y + parameters_Y*((48*parameters_p - 12*parameters_m +
36)/parameters_Gb - 5) - 1)*H2O
+ (- parameters_Y - parameters_Y*((36*parameters_p - 12*parameters_n +
24)/parameters_Gb - 4) + 1)*H
+ (-parameters_Y*(12/parameters_Gb - 2))*CO3
+ (-(12*parameters_Y*parameters_n)/parameters_Gb)*NH4
+ (-(12*parameters_Y*parameters_p)/parameters_Gb)*PO4
- 2*H2*(parameters_Y - 1)
```

7.4.7 *Methanol Methanogenesis Growth*

```
ProductCoeff =

(6*parameters_Ymm)/parameters_Gb*Zmm - MeOH
+     (parameters_Ymm*((24*parameters_p     -     6*parameters_m     +
18)/parameters_Gb - 2) - parameters_Ymm/4 + 1/4)*H2O
+   (1/2   -   parameters_Ymm*((18*parameters_p   -   6*parameters_n   +
12)/parameters_Gb - 2) - parameters_Ymm/2)*H
+ (1/4 - parameters_Ymm*(6/parameters_Gb - 1) - parameters_Ymm/4)*CO3
-((6*parameters_n*parameters_Ymm)/parameters_Gb)*NH4
-((6*parameters_p*parameters_Ymm)/parameters_Gb)*PO4
+ (3/4 - (3*parameters_Ymm)/4)*CH4
```

7.4.8 *Acetoclastic Methanogenesis Growth*

ProductCoeff =

```
((8*parameters_Y)/parameters_Gb)*BIOMASS - Ac
+ (- 3*parameters_Y + (8*parameters_Y*(4*parameters_p - parameters_m +
3))/parameters_Gb - 1)*H2O
+ (2*parameters_Y - (8*parameters_Y*(3*parameters_p - parameters_n +
2))/parameters_Gb + 1)*H
+ (parameters_Y - (8*parameters_Y)/parameters_Gb + 1)*CO3
+ (-(8*parameters_Y*parameters_n)/parameters_Gb)*NH4
+ (-(8*parameters_Y*parameters_p)/parameters_Gb)*PO4
+ (1 - parameters_Y)*CH4
```

7.4.9 *Hydrogenotrophic Methanogenesis Growth*

```
ProductCoeff =

+ ((2*parameters_Yhm)/parameters_Gb)*Zhm - H2
+ ((parameters_Yhm*(8*parameters_p - 2*parameters_m + 6))/parameters_Gb
- (3*parameters_Yhm)/4 + 0.75)*H2O
+ (parameters_Yhm/2 - (parameters_Yhm*(6*parameters_p - 2*parameters_n
+ 4))/parameters_Gb - 0.5)*H
+ (parameters_Yhm/4 - (2*parameters_Yhm)/parameters_Gb - 0.25)*CO3
-((2*parameters_n*parameters_Yhm)/parameters_Gb)*NH4
-((2*parameters_p*parameters_Yhm)/parameters_Gb)*PO4
+ (0.25 - parameters_Yhm/4)*CH4
```

7.4.10 *Urea Hydrolysis*

NB: not code generated, as per AD-FTRW1, with necessary component transformations

ProductCoeff =

```
-Urea - 2*H2O + CO3 +2*NH4
```

7.4.11 *Formate Digestion Growth*

```
ProductCoeff =

((2*parameters_Y)/parameters_Gb)*BIOMASS - Fmt
+ (parameters_Y + parameters_Y*((8*parameters_p - 2*parameters_m +
6)/parameters_Gb - 1) - 1)*H2O
+ (- parameters_Y - parameters_Y*((6*parameters_p - 2*parameters_n +
4)/parameters_Gb - 1) + 1)*H
```

+ (1 - parameters_Y*(2/parameters_Gb - 1) - parameters_Y)***CO3**

```
+ (-(2*parameters_Y*parameters_n)/parameters_Gb)*NH4
```

+ (-(2*parameters_Y*parameters_p)/parameters_Gb)***PO4**

```
+ (1 - parameters_Y)*H2
```

7.5 Model Constants

7.5.1 *AD-FTRW1*

AD-FTRW1		
Name	**Value**	**Description**
bacBu	0.015	ZacBu Endogenous Respiration Rate [1/d]
bacEt	0.015	ZacEt Endogenous Respiration Rate [1/d]
bacHx	0.015	ZacHx Endogenous Respiration Rate [1/d]
bacPr	0.015	ZacPr Endogenous Respiration Rate [1/d]
bacVa	0.015	ZacVa Endogenous Respiration Rate [1/d]
bad	0.041	Zad Endogenous Respiration Rate [1/d]
bam	0.037	Zam Endogenous Respiration Rate [1/d]
bhm	0.01	Zhm Endogenous Respiration Rate [1/d]
bmm	0.37	Zmm Endogenous Respiration Rate [1/d]
f	0.008	Unbiodegradable Frational of Biomass
FacBu	0.081831824755152	Dissociated Fraction of But In Influent
FacHx	0.0767893196971003	Dissociated Fraction of Hxt In Influent
FacPr	0.0735875561175735	Dissociated Fraction of Prt In Influent
FacVa	0.0853592420994873	Dissociated Fraction of Vat In Influent
Fam	0.0473936979865981	Apparent Total Dissociated Fraction of Act
FamIn	0.0947873959731961	Dissociated Fraction of Act In Influent
KAc	1.77827941003892E-5	HAc/Ac Weak Acid Dissociation Constant
KBu	1.51356124843621E-5	HBu/Bu Weak Acid Dissociation Constant
Kc1	4.96426538013667E-7	H2CO3/HCO3 Weak Acid Dissociation Constant
Kc2	5.75016967547348E-11	HCO3/CO3 Weak Acid Dissociation Constant
Kco2	0.02373	CO2 Equilibruim Constant
Kfco2	500	CO2 Expulsion/Dissolusion Rate [1/d]
Kh	0.024673218570212	Henry's Law Constant
KHx	1.41253754462276E-5	HHx/Hx Weak Acid Dissociation Constant (-log)
KHydrox	1000	OH to HCO3 Conversion Rate
kIAtZacPr	0.018	At Inhibition Constant for ZacPr
kIAtZam	0.1	At Inhibtion Constant for Zam
kIH2Zac	1E-5	Disolved H2(gas) Inhibition constant for all Zac except ZacPr
kIH2ZacPr	3.5E-6	Disolved H2(gas) Inhibition constant for ZacPr
kIH2Zad	0.000625	Disolved H2(gas) Inhibition constant for Zad
KPr	1.34896288259165E-5	HPr/Pr Weak Acid Dissociation Constant
KsacBu	0.003125	Half Saturation Constant ZacBu [mol/L]
KsacEt	0.000128	Half Saturation Constant ZacEt [mol/L]
KsacHx	0.0066	Half Saturation Constant ZacHx [mol/L]
KsacPr	0.01023	Half Saturation Constant ZacPr [mol/L]
KsacVa	0.00186	Half Saturation Constant ZacVa [mol/L]
Ksad	0.00666	Half Saturation Constant Zad [mol/L]
Ksam	0.0145	Half Saturation Constant Zam [mol/L]
Kshm	0.0006	Half Saturation Constant Zad [mol/L]
Ksmm	0.0145	Half Saturation Constant Z [mol/L]
KUrea	4.5	Urea to NH4 Conversion Rate
KVa	1.58489319246111E-5	HVa/Va Weak Acid Dissociation Constant
pHfeed	3.77	Influent pH
pHLLZadZac	4	Lower pH of 50% Inhibition for Zad & Zac
pHLLZamZmm	6.5	Lower pH of 50% Inhibition for Zam & Zmm
pHLLZhm	6.5	Lower pH of 50% Inhibition for Zhm
pHULZadZac	8	Upper pH of 50% Inhibition for Zad & Zac
pHULZamZmm	8	Upper pH of 50% Inhibition for Zam & Zmm
pHULZhm	8	Upper pH of 50% Inhibition for Zhm
Tk	310	Reactor Temperature [Kelvin]

TLL	305	Lower Temperature of 50% Inhibition
TUL	315	Upper Temperature of 50% Inhibition
UmaxacBu	2.268	Maximum Specific Growth Rate ZacBu [1/d]
UmaxacEt	1.15	Maximum Specific Growth Rate ZacEt [1/d]
UmaxacHx	1.18	Maximum Specific Growth Rate ZacHx [1/d]
UmaxacPr	1.1	Maximum Specific Growth Rate ZacPr [1/d]
UmaxacVa	1.53	Maximum Specific Growth Rate ZacVa [1/d]
Umaxad	0.8	Maximum Specific Growth Rate Zad [1/d]
Umaxam	1.15	Maximum Specific Growth Rate Zam [1/d]
Umaxhm	1.2	Maximum Specific Growth Rate Zhm [1/d]
Umaxmm	1.15	Maximum Specific Growth Rate Zmm [1/d]
YacBu	0.0558	ZacBu Stoichiometric Biomass Yield [mol_biomass/mol_Bu]
YacEt	0.0832	ZacEt Stoichiometric Biomass Yield [mol_biomass/mol_EtOH]
YacHx	0.0474	ZacHx Stoichiometric Biomass Yield [mol_biomass/mol_Hx]
YacPr	0.0376	ZacPr Stoichiometric Biomass Yield [mol_biomass/mol_Pr]
YacVa	0.0496	ZacVa Stoichiometric Biomass Yield [mol_biomass/mol_Va]
Yad	0.1074	Zad Stoichiometric Biomass Yield [mol_biomass/mol_Sbp]
Yam	0.0157	Zam Stoichiometric Biomass Yield [mol_biomass/mol_Ac]
Yhm	0.004	Zhm Stoichiometric Biomass Yield [mol_biomass/mol_H2]
Ymm	0.0127	Zmm Stoichiometric Biomass Yield [mol_biomass/mol_MeOH]
Number of Parameters	**70**	

7.5.2 *AD-FTRW2*

AD-FTRW2		
Name	**Value**	**Description**
bacBu	0.015	ZacBu Endogenous Respiration Rate [1/d]
bacEt	0.015	ZacEt Endogenous Respiration Rate [1/d]
bacHx	0.015	ZacHx Endogenous Respiration Rate [1/d]
bacPr	0.015	ZacPr Endogenous Respiration Rate [1/d]
bacVa	0.015	ZacVa Endogenous Respiration Rate [1/d]
bad	0.041	Zad Endogenous Respiration Rate [1/d]
bam	0.037	Zam Endogenous Respiration Rate [1/d]
bfd	0.01	Zfd Endogenous Respiration Rate [1/d]
bhm	0.01	Zhm Endogenous Respiration Rate [1/d]
bmm	0.37	Zmm Endogenous Respiration Rate [1/d]
CO2exponent	1	Exponent for CO2 expulsion
conc_mol_conversion(Ac_)	0.0169364932313305	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(Bu_)	0.011481412167771	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(Cl_)	0.0282063577130285	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(CO3_)	0.0166641670416104	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(Fo_)	0.0222135836063753	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(Hx_)	0.00868428708516246	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(H_)	0.992161920825479	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(Na_)	0.0434971726837756	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(NH4_)	0.0554375966693092	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(PO4_)	0.0105294857188585	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(Pr_)	0.0136853759441199	Conversion factor kg/m3 --->mol/l
conc_mol_conversion(Va_)	0.00988885911243534	Conversion factor kg/m3 --->mol/l
f	0.008	Unbiodegradable fraction of biomass
Gb	4	Biomass electron-accepting capacity
Kco2	0.02373	CO2 Equilibruim Constant
Kfco2	500	CO2 Expulsion/Dissolusion Rate [1/d]

Kh	11.6846436239017	Henry's Law Constant
kIAtZacPr	0.018	At Inhibition Constant for ZacPr
kIAtZam	0.1	At Inhibtion Constant for Zam
kIH2Zac	1E-5	Dissolved H2(gas) Inhibition constant for all Zac except ZacPr
kIH2ZacPr	3.5E-6	Disolved H2(gas) Inhibition constant for ZacPr
kIH2Zad	0.000625	Dissolved H2(gas) Inhibition constant for Zad
KsacBu	0.003125	Half Saturation Constant ZacBu [mol/L]
KsacEt	0.000128	Half Saturation Constant ZacEt [mol/L]
KsacHx	0.0066	Half Saturation Constant ZacHx [mol/L]
KsacPr	0.01023	Half Saturation Constant ZacPr [mol/L]
KsacVa	0.00186	Half Saturation Constant ZacVa [mol/L]
Ksad	0.00666	Half Saturation Constant Zad [mol/L]
Ksam	0.0145	Half Saturation Constant Zam [mol/L]
Ksfd	0.05	Half Saturation Constant Zfd [mol/L]
Kshm	0.0006	Half Saturation Constant Zad [mol/L]
Ksmm	0.0145	Half Saturation Constant Zmm [mol/L]
KUrea	4.5	Urea to NH4 Conversion Rate
l	1.4	Biomass Formula C(1)H(l)O(m)N(n)P(p)
m	0.4	Biomass Formula C(1)H(l)O(m)N(n)P(p)
n	0.2	Biomass Formula C(1)H(l)O(m)N(n)P(p)
p	0	Biomass Formula C(1)H(l)O(m)N(n)P(p)
pHLLZadZac	4	Lower pH of 50% Inhibition for Zad & Zac
pHLLZamZmmZhm	6.5	Lower pH of 50% Inhibition for Zam & Zmm
pHULZadZac	8	Upper pH of 50% Inhibition for Zad & Zac
pHULZamZmmZhm	8	Upper pH of 50% Inhibition for Zam & Zmm
Tk	310	Reactor Temperature [Kelvin]
TLL	305	Lower Temperature of 50% Inhibition
TUL	315	Upper Temperature of 50% Inhibition
UmaxacBu	2.268	Maximum Specific Growth Rate ZacBu [1/d]
UmaxacEt	1.15	Maximum Specific Growth Rate ZacEt [1/d]
UmaxacPr	1.1	Maximum Specific Growth Rate ZacPr [1/d]
UmaxacVa	1.53	Maximum Specific Growth Rate ZacVa [1/d]
Umaxad	0.8	Maximum Specific Growth Rate Zad [1/d]
Umaxam	1.15	Maximum Specific Growth Rate Zam [1/d]
Umaxfd	1.1	Maximum Specific Growth Rate Zfd [1/d]
Umaxhm	1.2	Maximum Specific Growth Rate Zhm [1/d]
Umaxmm	1.15	Maximum Specific Growth Rate Zmm [1/d]
Yacbu	0.0558	ZacBu Stoichiometric Biomass Yield [mol biomass/mol Bu]
Yacet	0.0832	ZacEt Stoichiometric Biomass Yield [mol biomass/mol Et]
Yachx	0.0474	ZacHx Stoichiometric Biomass Yield [mol biomass/mol Hx]
Yacpr	0.0376	ZacPr Stoichiometric Biomass Yield [mol biomass/mol Pr]
Yacva	0.0496	ZacVa Stoichiometric Biomass Yield [mol biomass/mol Va]
Yad	0.1074	Zad Stoichiometric Biomass Yield [mol biomass/mol Sbp]
Yam	0.0157	Zam Stoichiometric Biomass Yield [mol biomass/mol Ac]
Yfd	0.015	Zfd Stoichiometric Biomass Yield [mol biomass/mol H2]
Yhm	0.004	Zhm Stoichiometric Biomass Yield [mol biomass/mol H2]
Ymm	0.0127	Zmm Stoichiometric Biomass Yield [mol biomass/mol MeOH]
Number of Parameters	**74**	

7.6 Gujer Matrix of AD-FTRW1

A Gujer Matrix representing the dynamic AD-FTRW1 model stoichiometry is presented in Figure 16 below. The model components are displayed in the columns across the top from H_2O to Z_{xx} while the 21 model processes can be seen in the rows. The growth processes are shown in the uneven rows numbered 1 to 17, with the death processes presented by the even numbered processes 2 to 18.

In order to fit the Gujer Matrix onto a single A4 page for ease of reference, certain unorthodox formatting techniques were employed in the table. Firstly, all even numbered processes (which are representative of death processes) have been greyed out/omitted due to the fact that their stoichiometry is the same for each FOG. It was therefore considered repetitive and unnecessary to depict each death process in the matrix below. Secondly, a composite component (Z_{xx}) is used to condense the table further; the meaning of which is explained in the subsequent paragraphs.

Where the "xx" subscript is adopted to denote the biomass of each FOG separately and so can take on the following labels explained in the LIST OF ACRONYMS/A: ad, acHx, acVa, acBu, acPr, acEt, mm, am and hm. This is in-line with the use of Z_{xx} (a composite component) in Figure 16 below where this single column represents multiple model components (components 18 to 26) in order to condense the matrix even further. Z_e (endogenous residue), the 27th model component in the actual Gujer Matrix for AD-FTRW1, is not shown in the matrix below. This is due to the fact that it is involved only in the death processes which, as was previously mentioned, have been excluded from this Gujer Matrix representation.

Figure 16: Gujer matrix representation of AD-FTRW1

Components	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	...		
Processes	H_2O	CH_4	H_2	CO_2	H_2CO_3	HCO_3^-	NH_4^+	Ac	MeOH	EtOH	Pr	Bu	Va	Hx	$(NH_2)_2CO$	OH^-	S_{bp}	Z_{ax}	...	Components
1 ad	$\frac{-5(1-Y_{ad})}{Y_{ad}}$		$\frac{2(1-Y_{ad})}{Y_{ad}}$			$\frac{(1-Y_{ad})}{Y_{ad}}$	$\frac{(1-Y_{ad})}{Y_{ad}}$	$\frac{2(1-Y_{ad})}{Y_{ad}}$									$\frac{-1}{Y_{ad}}$	1	Z_{ad}	18
3 acHx	$\frac{-(10-34Y_{acHx})}{8Y_{acHx}}$		$\frac{8(1-Y_{acHx})}{8Y_{acHx}}$		$\frac{-(5F_{acHx}+2Y_{acHx})}{8Y_{acHx}}$	$\frac{(5F_{acHx}-8Y_{acHx})}{8Y_{acHx}}$	-1	$\frac{5(1-Y_{acHx})}{8Y_{acHx}}$				$\frac{5(1-Y_{acHx})}{8Y_{acHx}}$		$\frac{-5}{8Y_{acHx}}$				1	Z_{acHx}	19
5 acVa	$\frac{-(20-59Y_{acVa})}{13Y_{acVa}}$		$\frac{20(1-Y_{acVa})}{13Y_{acVa}}$		$\frac{-(10F_{acVa}+2Y_{acVa})}{13Y_{acVa}}$	$\frac{(10F_{acVa}-13Y_{acVa})}{13Y_{acVa}}$	-1	$\frac{10(1-Y_{acVa})}{13Y_{acVa}}$			$\frac{10(1-Y_{acVa})}{13Y_{acVa}}$		$\frac{-10}{13Y_{acVa}}$					1	Z_{acVa}	20
7 acBu	$\frac{-(2-5Y_{acBu})}{13Y_{acBu}}$		$\frac{2(1-Y_{acBu})}{Y_{acBu}}$		$\frac{-F_{acBu}}{Y_{acBu}}$	$\frac{F_{acBu}}{Y_{acBu}}-1$	-1	$\frac{2(1-Y_{acBu})}{Y_{acBu}}$				$\frac{-1}{Y_{acBu}}$						1	Z_{acBu}	21
9 acPr	$\frac{-(30-51Y_{acPr})}{7Y_{acPr}}$		$\frac{30(1-Y_{acPr})}{7Y_{acPr}}$		$\frac{(10-8Y_{acPr}-10F_{acPr})}{-7Y_{acPr}}$	$\frac{(10F_{acPr}-7Y_{acPr})}{7Y_{acPr}}$	-1	$\frac{10(1-Y_{acPr})}{7Y_{acPr}}$			$\frac{-10}{7Y_{acPr}}$							1	Z_{acPr}	22
11 acEt	$\frac{-5(5-19Y_{acEt})}{15Y_{acEt}}$		$\frac{10(1-Y_{acEt})}{3Y_{acEt}}$		$\frac{-2}{3}$	-1	-1	$\frac{5(1-Y_{acEt})}{3Y_{acEt}}$		$\frac{-5}{3Y_{acEt}}$								1	Z_{acEt}	23
13 mm	$\frac{(5-33Y_{mm})}{6Y_{mm}}$	$\frac{(30-30Y_{mm})}{12Y_{mm}}$			$\frac{-(5-9Y_{mm})}{6Y_{mm}}$	-1	-1		$\frac{-10}{3Y_{mm}}$									1	Z_{mm}	24
15 am	$\frac{-(5-11Y_{am})}{2Y_{am}}$	$\frac{(5-5Y_{am})}{2Y_{am}}$			$\frac{(5-3Y_{am}-5F_{am})}{2Y_{am}}$	$\frac{(5F_{am}-2Y_{am})}{2Y_{am}}$	-1	$\frac{-5}{2Y_{am}}$										1	Z_{am}	25
17 hm	$\frac{10(15+11Y_{hm})}{-20Y_{hm}}$	$\frac{(10-10Y_{hm})}{4Y_{hm}}$	$\frac{-10}{Y_{hm}}$		$\frac{-10(5-3Y_{hm})}{20Y_{hm}}$	-1	-1											1	Z_{hm}	26
19 ...	1			1	-1															
20 ...	1				-1	1										-1				
21 ...	-2				-1	2	2								-1					

7.7 Henry's Law Constant Calculation

It was decided to apply, pseudo-equilibrium Henry's Law kinetics to describe Carbon dioxide Expulsion/Dissolution. The stoichiometry for this process is given by:

Process Reaction

$$H_2CO_3(aq) \rightarrow CO_2 + H_2O$$

The model kinetics are described as:

$$r = K_{fCO2}\left([H_2CO_3] - K_h\frac{[CO_2]}{[CO_2]+[CH_4]}\right)$$

The Henry's law constant was sourced from the minteqA2 database but since it did not have it in the form in which it was applied in AD-FTRW1&2, the constant required some manipulation from constituent reactions. The calculation of the constant used is outlined below.

Constituent Reaction 1

$$CO_3^{2-} + 2H^+ \leftrightarrow H_2CO_3$$

$$\log K_1 = 16.681$$

$$\Delta H_1 = -23.76\ kJ$$

Constituent Reaction 2

$$CO_2(g) + H_2O \leftrightarrow 2H^+ + CO_3^{2-}$$

$$\log K_2 = -18.147$$

$$\Delta H_2 = 4.06\ kJ$$

Since the Process reaction is the sum of the reverse constituent reactions,

$$Process\ Reaction = -Constituent\ Reaction\ 1 - Constituent\ Reaction\ 2$$

the process reaction constants were determined as follows;

$\log K_p = -\log K_1 - \log K_2 = 1.466$ @25°C

$\Delta H_k = -\Delta H_1 - \Delta H_2 = 19.7\ kJ$

Equilibrium constants are largely temperature dependent and since the Mesophilic Anaerobic Digestion System operates at 37°C, it was necessary to determine the equilibrium constant for that temperature. The temperature dependence of reaction constants is generally described via the Van't Hoff Equation which states that;

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

Where:

$R = 8.314$ J/mol/K

Taking $K_1 = K_p \quad T_1 = 298K \; and \; T_2 = 310K$ this yields a Henry's Law constant of 39.62 (atm.l/mol) or 0.02524 (mol/l/atm)

$\therefore K_h = 0.02524 \; (\frac{mol}{l.atm})$

It was then realised that CO_2 and CH_4 were not the only gases present in the vapour space of the digester. At 37°C , a significant partial pressure of water vapour would exist. This is given by the vapour pressure of water at 37°C and 1 atm and can be determined from the Antoine equation which reads as follows:

$\log p = A - \frac{B}{C+T}$

Where for water $A = 8.07131$, $B = 1730.63 \; and \; C = 233.426$

And the constants are relevant to temperature in °C and pressure in mmHg. The application of this equation at 37°C yields a vapour pressure of $p_{H_2O\,(v)} = 0.07$ atm.

This meant that the partial pressure of CO_2 had to be adjusted to account for the existence of water vapour in the head-space. The adaptation of the kinetics to account for this phenomenon is shown from the original starting point

6) $r = K_{fCO2}\left([H_2CO_3] - K_h p_{CO_2}\right)$
7) $r = K_{fCO2}\left([H_2CO_3] - K_h \frac{[CO_2]}{[CO_2]+[CH_4]}\right)$
8) $r = K_{fCO2}\left([H_2CO_3] - K_h.\left(1 - p_{H_2O\,(v)}\right).\frac{[CO_2]}{[CO_2]+[CH_4]}\right)$

Where 1 represents $1\,atm$ which is the total pressure of the system and therefore $\left(1 - p_{H_2O\,(v)}\right)$ represents the partial pressure that can be attributed to CO_2 and CH_4.

Instead of introducing more parameters into the model to account for the partial pressure of water vapour, it was decided to lump these effects into the Henry's law constant:

9) $K_h^{H_2O(v)} = K_h.\left(1 - p_{H_2O\,(v)}\right) = 0.02524 \times (1 - 0.07) = 0.023473 \; \frac{mol}{l}$

This yielded the finalized kinetics of:

$$10)\ r = K_{fCO2}\left([H_2CO_3] - K_h^{H_2O(v)}\frac{[CO_2]}{[CO_2]+[CH_4]}\right)$$

7.8 pKa vs Carbon Number for SCFA's

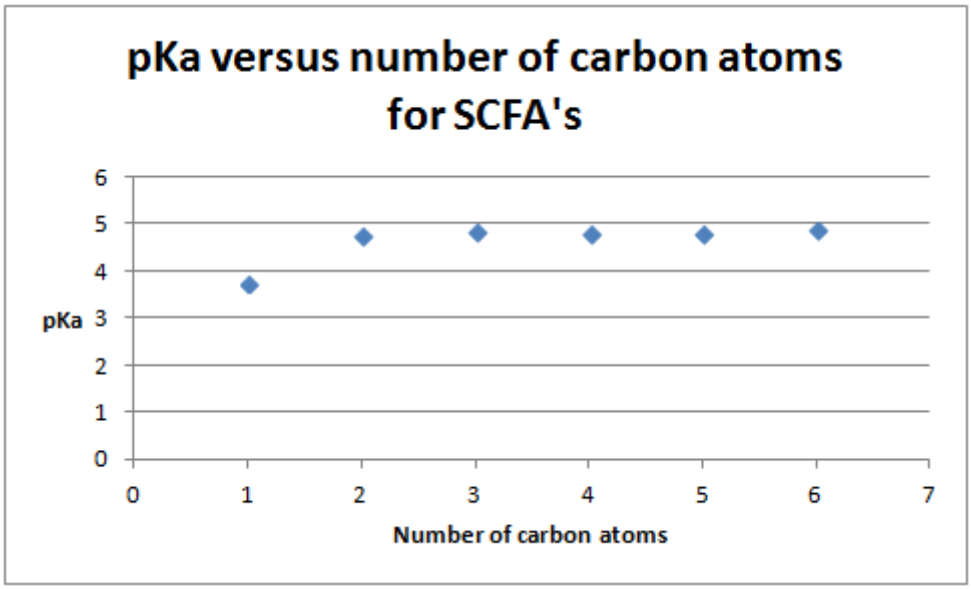

Figure 17: pKa vs Carbon Number for SCFA's

7.9 Ionic Speciation Subroutine Code

```
// #define DLL_EXPORT
#include  <math.h>
#include  <stdlib.h>
#include  <malloc.h>
#include  <float.h>

extern "C"
{
        double conduct(int Species_Count, double c[], double charge[], double* Tk, double* I, double
Lo[])
{
        double vis ;
   // Limiting ion molar conductivities at 25 deg C
        // Calculated from diffusivities Dw in PHREEQC database
        // Estimated values for ion pairs without data.
```

```
        // Combined limiting conductivity
        double L = 0.0 ;  // cations
        double La = 0.0 ;  // anions
        double ct = 0.0 ;  // total concentration
  for ( int ii=0 ; ii < Species_Count ; ii++)
        {
                if (charge[ii] > 0.1)  {L = L + Lo[ii]*c[ii] ; }
                if (charge[ii] < -0.1) {La = La + Lo[ii]*c[ii] ; }
                ct = ct + c[ii] ;
        }
        L = 4.0*L*La/(L+La) ;
 // Ionic strength correction
        L = L - 27.606*pow(*I,1.28) - 1.135*pow(ct,2.3333);
 // Viscosity of water
        vis = (*Tk)-293.15;
        if ((*Tk) < 293.15)
        {
          vis = 1301.0/(998.333+8.1855*vis+0.00585*vis*vis)-1.30233 ;
          vis = pow(10,vis) ;
        }
        else
        {
                vis = (-1.3272*vis-0.001053*vis*vis)/((*Tk)-168.15) ;
                vis = 1.002*pow(10,vis) ;
        }
 // Viscosity correction
        L = L*pow((0.890469539/vis),0.896) ;
        return L ;
}

// ____________________________________________________________________


 void kthermo(double* Tk, int Species_Count,
                                        double logK[], double deltaH[], double kt[],
                                        double* Adh)
{

/*
 *   compute temperature dependence of A and b for debye-huckel (copied from PHREEQC: model.c)
```

```
 */
  double s1 = 647.26 - (*Tk) ;
  double s2 = pow (s1, 1.0 / 3.0);
  double s3 = 1.0 + 0.1342489 * s2 - 3.946263e-03 * s1;
  s3 =
    s3 / (3.1975 - 0.3151548 * s2 - 1.203374e-03 * s1 +
          7.48908e-13 * (s1 * s1 * s1 * s1));
  s3 = sqrt (s3);
  if ((*Tk) >= 373.15)
  {
    *Adh =
      5321.0 / (*Tk) + 233.76 - (*Tk) * ((*Tk) * (8.292e-07 * (*Tk) - 1.417e-03) +
                                         0.9297);
  }
  else
  {
    *Adh =
      2727.586 + 0.6224107 * (*Tk) - 466.9151 * log ((*Tk)) - 52000.87 / (*Tk);
  }
  s1 = sqrt (*Adh * (*Tk));

  *Adh = 1824827.7 * s3 / (s1 * s1 * s1);
//  b = 50.2905 * s3 / c1;

// calculate thermodynamic (infinite dilution) equilibrium constants
  // LogK = logK(25C) - DeltaH * Tcorrection ; DeltaH in joules/mol
        double Tcorrection = (1/(*Tk) - 1/298.15)/(2.303*8.314) ;
        for (int i=0 ; i<Species_Count ; i++)
        {
                kt[i]=pow(10.0,(logK[i]-deltaH[i]*Tcorrection)) ;
        }
}

// ____________________________________________________________________


// Routine to calculated ionic strength
         double IonicStrength(int Species_Count, double c[], int charge[])
{
        double result = c[0] ;
```

```
    for (int is=1 ; is < Species_Count ; is++)
        result = result + c[is]*charge[is]*charge[is] ;
    return 0.5*result ;
}
// ____________________________________________________________________


// Routine to calculated activity coefficients from ionic strength
// Also returns activity od water
    void ActivityCoefficients(int Species_Count,
                                                                    double c[], int charge[],
double gamma[],
                                                                    double I, double* Adh,
double* actwater )
{
            int is ;
            double gam[4] ;
            // Ionic strength calculation

   double sqI = sqrt(I) ;
   gam[0] = 0.1*(I) ;
   gam[1] = -(*Adh) *(sqI/(1+sqI)-0.3*I) ;
   gam[2]=4.0*gam[1] ;
   gam[3]=9.0*gam[1] ;
   for (is=0 ; is < 4 ; is++) { gam[is]=pow(10,gam[is]); }

   // Activity coefficients of all species plusd activity of water
    *actwater = 2.0*((*Adh) * (1.0 + sqI - 2.0*log(1.0+sqI) - 1.0/ (1.0+sqI))) - 0.079*I*I;
            *actwater = (*actwater) * 2.302585093 ;

            for ( is = 0 ; is < Species_Count ; is++)
     {
        gamma[is] = gam[abs(charge[is])] ;
                        *actwater = (*actwater) - c[is];
     }
    *actwater = exp((*actwater)/55.509914) ;

    return ;
}
//____________________________________________________________________
```

```
// routine to calculate linear compbinations of concentrations
   double Composite(double conc[], int Stoi[])
  {
            double result = 0.0 ;
            for (int i=0 ; i<Stoi[0]; i++)
                     result = result+conc[Stoi[i*2+1]]*Stoi[i*2+2] ;
     return result ;
  }

//_____________________________________________________________________

// routine to calculate the error in the component mass balances
// for a trial set of master species concentrations
// (which are H to HPO4)
 double TrySpeciation(double logValue, double* Adh,
       int Component_Count, double tot[],
                     int balance[], int BalanceCoef[], int BalanceMap[], int NonMaster[],
                     int Species_Count, double c[], int charge[], double k[], double gamma[],
                     int SpeciesID[], int Stoichiometry[], int SpeciesMap[],
       double* I,  double* actwater, double* residerr)
{
          double divisor[25], factor, newc[25] ;
          int ii, ic, is, kk, bstart, bnext, sstart, snext, js, im ;

   double remem=c[0] ;
          c[0] = pow(10,logValue) ;  // Trial concentration of H+
          // Component balances
          for ( ic=1 ; ic < Component_Count ; ic++ )  // Balance the other components apart from H+
    {
                    bstart = BalanceMap[ic] ; bnext = BalanceMap[ic+1] ;
                    im = balance[bstart] ;  // master species for component ic
                    divisor[ic]=0 ;
     for ( ii=bstart+1 ; ii < bnext ; ii++)
                    {
                              is = balance[ii];              // index of species in balance
                              factor = k[is]*BalanceCoef[ii] ;  // balance coefficient of species
                              sstart = SpeciesMap[is] ; snext = SpeciesMap[is+1] ;
                              for (kk=sstart ; kk < snext ; kk++)
                              {
```

```
                                        js = SpeciesID[kk] ;        // index of master species in formation of
species[is]
                                        if (js != im)               // skip if master species
                                        {
                                                factor = factor * pow((c[js]*gamma[js]),Stoichiometry[kk])
;
                                        }
                                }
                        divisor[ic] = divisor[ic]+factor/gamma[is] ;
                }
        divisor[ic]=divisor[ic]*gamma[im]+BalanceCoef[bstart] ; // add master species contibution ;
        }
    //Recalculate concentrations of master species
     newc[0] = pow(10.0,logValue) ;
        for ( ic=1 ; ic < Component_Count ; ic++)
    {
                newc[ic] = tot[ic]/divisor[ic] ;
        }

  // Update concentrations of master species and
  // calculate error between new results and last iteration results

        *residerr = 0 ;
        double Error ;
        for ( ic=1 ; ic < Component_Count ; ic++)
        {
                im = balance[BalanceMap[ic]] ;  // master species for component ic
                if (fabs(newc[ic]) < 1.0e-9)
                        {Error = 0.0 ;}
           else
                        {Error = 1.0 - c[im]/(newc[ic]) ;}

                *residerr = *residerr+fabs(Error) ;
                 c[im] = newc[ic] ;
        }

        // Fill in remaining species concentrations
    for ( kk=0 ; kk < Species_Count-Component_Count ; kk++)
        {
                is = NonMaster[kk] ;
```

```
                factor = k[is]/gamma[is] ;
                sstart = SpeciesMap[is] ; snext = SpeciesMap[is+1] ;
                for (ii=sstart ; ii < snext ; ii++)
                {
                        js = SpeciesID[ii] ;      // index of master species in formation of species[is]
                        factor = factor * pow((c[js]*gamma[js]),Stoichiometry[ii]) ;
                }
                c[is] = factor ;
        }

        // Now H balance
        // H+ must be first component
        bstart = BalanceMap[0] ; bnext = BalanceMap[1] ;
        factor = 0.0 ;
  for (ii=bstart ; ii<bnext ; ii++)
        {
                is = balance[ii] ;
                factor = factor + c[is]*BalanceCoef[ii] ;  // balance coefficient of species
  }

        Error= factor - tot[0] ;



return Error  ;

}

// ____________________________________________________________________

// Speciate a set of total concentrations to give species concentrations
// H+ must be first component (tot[0]) and first species (c[0])
 double speciate(double tot[], double c[], double gamma[], double k[],
                double* Tk, double* lastTk, double* Adh,
                                                double* I, double* pHeq, double* actwater,
                                                double* test1, double* test2)
{
  // The following arrays define the speciation model stoichiometry and thermodynamics
  // for components: H, Fo, Ac, Pr, HOrg, NH4, PO4, NO3, CO3, Na, Cl
  // and species: H,Fo,Ac,Pr,HOrg,NH4,HPO4,NO3,HCO3,Na,Cl,OH,CO3,H2CO3,NaCO3,NaHCO3,
```

```
 // H2PO4,NaHPO4,HFo,HAc,NaAc,HPr,HHOrg,NH3.

//_____________________________________________________________________________
___
  static int Component_Count = 12 ; static int Species_Count = 28 ;
//_____________________________________________
static                                                                    int
balance[45]={0,8,9,12,14,16,17,18,19,20,22,23,24,25,26,9,13,14,15,16,7,26,8,17,18,27,6,25,5,24,4,23,3,
22,2,20,21,1,19,10,15,16,18,21,11} ;
static                int                BalanceCoef[45]={1,1,1,-1,2,1,2,1,1,1,1,1,1,1,-
1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1} ;
static int BalanceMap[13]={0,15,20,22,26,28,30,32,34,37,39,44,45} ;
static int NonMaster[16]={12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27} ;
static int charge[28]={1,-1,-1,-1,-1,-1,-1,1,-2,-1,1,-1,-1,-2,0,-1,0,-1,-1,0,0,0,0,0,0,0,0,-3} ;
static          double          logK[28]={0,0,0,0,0,0,0,0,0,0,0,0,-13.997,-10.329,6.352,-9.059,-
0.25,7.198,1.07,3.745,4.757,-0.18,4.784,4.819,4.843,4.85,-9.244,-12.375} ;
static          double          deltaH[28]={0,0,0,0,0,0,0,0,0,0,0,0,55810,14600,-9160,-5750,-13730.1,-
3000,15000,167.4,410,12000,660,2800,2887,2950,-52000,15000} ;
static                                                                    int
SpeciesID[44]={0,1,2,3,4,5,6,7,8,9,10,11,0,0,9,0,9,0,10,9,10,9,0,8,10,8,0,1,0,2,2,10,0,3,0,4,0,5,0,6,0,7,0,
8} ;
static                int                Stoichiometry[44]={1,1,1,1,1,1,1,1,1,1,1,1,-1,-1,1,1,1,-
1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,-1,1,-1,1} ;
static                                                                    int
SpeciesMap[29]={0,1,2,3,4,5,6,7,8,9,10,11,12,13,15,17,20,22,24,26,28,30,32,34,36,38,40,42,44} ;
//_____________________________________________________________________________
___
  static double tolerance = 5.0E-6 ;
  static int ii ;
  static bool FirstTime = false ;
  static double  newV, totH, error0, error, residual, logV0, logV1 ;

  *test1 = *I  ;
  *test2 = 0.0 ;
 // Test that not all total concentrations are zero
  for ( ii=0 ; ii < Component_Count ; ii++ )
  {
     *test2 = *test2+fabs(tot[ii]) ;
  }
  if (*test2 <= 0.0)
```

```
  {
     *I = -1.0 ;
            *pHeq = -1.1 ;
     return *test2 ;
  }

// Ionic strength is set to < 0.0 by the calling routine
//  as a signal that there are no previous estimates available
//  for the species concentrations

  if (*I <= 0.0)
  {
   FirstTime = true ;
            *I = 0.02;
            *actwater = 0.998 ;
           int ic ;
           for ( ii=0 ; ii < Species_Count ; ii++)
           {
                    c[ii] = 1.0e-8 ;
                    gamma[ii] = 0.82 ;
           }
   for ( ii=0 ; ii < Component_Count ; ii++)
   {
      ic = balance[BalanceMap[ii]] ;
                    c[ic] = tot[ii]*0.85 ;
   }
  }
  else FirstTime = false ;
  totH = *test2*1.0E-08 ;
  if (fabs(tot[0]) > totH) totH = tot[0] ;

  // Initialise solver loop
  if ( *Tk != *lastTk)   // if temperature has changed
  { *lastTk = *Tk ;
 // calculate thermodynamic (infinite dilution) equilibrium constants
   kthermo(Tk,Species_Count,logK,deltaH,k,Adh) ;
  }
  // Evaluate equation error at initial point
  if (FirstTime) logV0 =-(*pHeq) ; else  logV0 = log10(c[0]) ;
  if (_isnan(logV0)||logV0 > -3.0||logV0 < -9.0) logV0 = -7.0 ;
```

```
 error0 = TrySpeciation(logV0, Adh,
                                                Component_Count, tot,
                                                balance, BalanceCoef, BalanceMap, NonMaster,
                        Species_Count, c, charge, k, gamma,
                                                SpeciesID, Stoichiometry, SpeciesMap,
                                                I, actwater, &residual);
          // Update Ionic strength and activity coefficients
  *I = IonicStrength(Species_Count,c,charge) ;
          ActivityCoefficients(Species_Count, c, charge, gamma, *I, Adh, actwater) ;

if (( fabs(error0/totH) < tolerance) && (residual < tolerance))  // if the result is good enough already
 {
            *pHeq = -log10(c[0]*(gamma[0])) ;
    *test1 = 0.0 ; *test2 = error0 ;
    return residual ;
 }
if (FirstTime)
{
          if (error0 > 0)
                    logV1 = logV0 - 0.001 ;
          else
                    logV1 = logV0 + 0.001 ;
}
else
{
          logV1 = log10(tot[0]*c[0]/(error0+tot[0])) ;
}
          error = TrySpeciation(logV1, Adh,
                                                Component_Count, tot,
                                                balance, BalanceCoef, BalanceMap, NonMaster,
                        Species_Count, c, charge, k, gamma,
                                                SpeciesID, Stoichiometry, SpeciesMap,
                                                I, actwater, &residual);
          // Update Ionic strength and activity coefficients
  *I = IonicStrength(Species_Count,c,charge) ;
          ActivityCoefficients(Species_Count, c, charge, gamma, *I, Adh, actwater) ;

// Solver loop (secant search)

 int count= 0 ; int rowbase = 0 ;
```

```
while ((( fabs(error/totH) > tolerance) || (residual > tolerance) || (count < 1)) && count < 40 )
  {
                if (FirstTime)
                {
                        if (error0 == error)
                                { newV = 0.5*(logV0 +logV1); }
                        else
                                {newV = (logV1*error0 - logV0*error)/(error0-error) ;}
                        if ((newV-logV1) > 0.8) newV = logV1 + 0.8 ;
                        if ((logV1-newV) > 0.8) newV = logV1 - 0.8 ;
                        logV0 = logV1 ;
                        if (fabs(newV-logV1) > 0.5) logV1 = newV*0.8+logV0*0.2 ;
                        else logV1=newV ;
                }
                else
                {
                        logV0 = logV1 ;
                        logV1 = log10(tot[0]*c[0]/(error+tot[0])) ;
                }
                error0 = error ;
                error = TrySpeciation(logV1, Adh,
                                Component_Count, tot,
                                balance, BalanceCoef, BalanceMap, NonMaster,
        Species_Count, c, charge, k, gamma,
                                SpeciesID, Stoichiometry, SpeciesMap,
                                I, actwater, &residual);
                // Update Ionic strength and activity coefficients
                 *I = IonicStrength(Species_Count,c,charge) ;
                ActivityCoefficients(Species_Count, c, charge, gamma, *I, Adh, actwater) ;
                count = count+1 ;
        }

  *pHeq = -log10(c[0]*gamma[0]) ;
        // Alkalinity calculation
  *test1 = double(count) ; *test2 = error ; // diagnostic values
  return residual ;
}

// ____________________________________________________________________________
```

```
// Speciate a set of total concentrations with pH, Alkalinity and ionic strength as input
// H+ must be first component (tot[0]) and first species (c[0])
// AlkOption :  0 - total alkalinity, no ionic strength adjustment
//              1 - carbonate alkalinity, "       "       "
//              2 - as 0, but with ionic strength adjustment
//              3 - as 1,  "     "       "       "       "
 double pHAlkalinity(int AlkOption, double tot[], double newtot[], double c[], double gamma[],double k[],
                     double* Tk, double* lastTk, double* Adh,
                                                     double* I, double* pHeq, double* actwater,
                                     double* Alkalinity,
                                                     double* residual, double* test1, double* test2)
{
  // The following arrays define the speciation model stoichiometry and thermodynamics
  // for components: H, Fo, Ac, Pr, HOrg, NH4, PO4, NO3, CO3, Na, Cl
  // and species: H,Fo,Ac,Pr,HOrg,NH4,HPO4,NO3,HCO3,Na,Cl,OH,CO3,H2CO3,NaCO3,NaHCO3,
  // H2PO4,NaHPO4,HFo,HAc,NaAc,HPr,HHOrg,NH3.

//_____________________________________________________________________________
___
   static int Component_Count = 12 ; static int Species_Count = 28 ;
   static int ComponentCharge[12] = {1,-2,1,-3,-1,-1,-1,-1,-1,-1,1,-1} ;
   static int CarbAlkStoi[9] = {4,9,1,13,2,15,2,16,1} ;
   static int AlkStoi[19]= {9,1,2,3,2,0,-1,4,1,5,1,6,1,7,1,8,1,9,1} ;
   static int AdjustedComp[3] = {1,10,11} ;
//_____________________________________________
   static                                                                                    int
balance[45]={0,8,9,12,14,16,17,18,19,20,22,23,24,25,26,9,13,14,15,16,7,26,8,17,18,27,6,25,5,24,4,23,3,
22,2,20,21,1,19,10,15,16,18,21,11} ;
static                    int                    BalanceCoef[45]={1,1,1,-1,2,1,2,1,1,1,1,1,1,1,-
1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1} ;
static int BalanceMap[13]={0,15,20,22,26,28,30,32,34,37,39,44,45} ;
static int NonMaster[16]={12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27} ;
static int charge[28]={1,-1,-1,-1,-1,-1,-1,1,-2,-1,1,-1,-1,-2,0,-1,0,-1,-1,0,0,0,0,0,0,0,0,-3} ;
static              double              logK[28]={0,0,0,0,0,0,0,0,0,0,0,0,-13.997,-10.329,6.352,-9.059,-
0.25,7.198,1.07,3.745,4.757,-0.18,4.784,4.819,4.843,4.85,-9.244,-12.375} ;
static              double              deltaH[28]={0,0,0,0,0,0,0,0,0,0,0,0,55810,14600,-9160,-5750,-13730.1,-
3000,15000,167.4,410,12000,660,2800,2887,2950,-52000,15000} ;
```

```
static int SpeciesID[44]={0,1,2,3,4,5,6,7,8,9,10,11,0,0,9,0,9,0,10,9,10,9,0,8,10,8,0,1,0,2,2,10,0,3,0,4,0,5,0,6,0,7,0,8} ;
static int Stoichiometry[44]={1,1,1,1,1,1,1,1,1,1,1,-1,-1,1,1,1,-1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,-1,1,-1,1} ;
static int SpeciesMap[29]={0,1,2,3,4,5,6,7,8,9,10,11,12,13,15,17,20,22,24,26,28,30,32,34,36,38,40,42,44} ;
  static double tolerance = 1.0E-5 ;
//_____

___

  static double  newV, totH, logH, error0, error ;
  static double  CO3tot0, CO3tot1,adjust,adjust1,adjust2,Herr,Ifixed, Alkfixed, pHfixed ;
  static int ii ;
  // Remember input values to be matches
  Ifixed = *I ;  Alkfixed = *Alkalinity ; pHfixed = *pHeq ;
  *test1 = *I  ;
  *test2=0 ;
  newtot[0] = tot[0] ;

 // Test that not all total concentrations are zero
  for ( ii=1 ; ii < Component_Count ; ii++ )
  {
     *test2 = *test2+fabs(tot[ii]) ;
     newtot[ii]=tot[ii] ;
  }
  if (*test2 <= 0.0)
  {
     *I = -1.0 ;
            *pHeq = -1.0 ;
            *Alkalinity = -1.0 ;
     return 0.0 ;
  }
  totH = *test2*1.0E-08 ;
  if (fabs(*Alkalinity) > totH) totH = (*Alkalinity) ;

//  actwater must be set to < -4 by the calling routine
//  as a signal that there are no previous estimates available
//  for the species concentrations
```

```
  if (*actwater < 0.0)   // Signal that there are no initial estimates of concentration
  {
          for (ii=0 ; ii<Species_Count ; ii++)
                  c[ii] = 1.0E-9 ;
   tot[0] = 0.005 ;
          for ( ii=1 ; ii < Component_Count ; ii++)
                  c[balance[BalanceMap[ii]]] = tot[ii]*0.85 ; // initial guess of master species concs
  }

  // Correct any ion imbalance in the initial composition
          error = 0.0 ;
          for (ii=0 ; ii<Component_Count ; ii++)
                   error = error+tot[ii]*ComponentCharge[ii] ;
                  tot[AdjustedComp[1]]                    =                    tot[AdjustedComp[1]]-
0.5*error/ComponentCharge[AdjustedComp[1]] ;
                  tot[AdjustedComp[2]]                    =                    tot[AdjustedComp[2]]-
0.5*error/ComponentCharge[AdjustedComp[2]] ;

  // Initialise solver loop
  if ( *Tk != *lastTk)   // if temperature has changed
  { *lastTk = *Tk ;
 // calculate thermodynamic (infinite dilution) equilibrium constants
   kthermo(Tk,Species_Count,logK,deltaH,k,Adh) ;
  }
  ActivityCoefficients(Species_Count,c,charge,gamma,Ifixed,Adh,actwater) ;
  logH = -pHfixed-log10(gamma[0]) ;

  // Evaluate equation error at initial point
  CO3tot0 = tot[AdjustedComp[0]] ;  // Primary search variable
  Herr = TrySpeciation(logH, Adh, Component_Count, tot,
                                      balance, BalanceCoef, BalanceMap, NonMaster,
            Species_Count, c, charge, k, gamma,
                                      SpeciesID, Stoichiometry, SpeciesMap,
                                      I, actwater, residual);
  tot[0] = tot[0]+Herr;   // adjust H+ total concentration
  if (AlkOption==0||AlkOption==2)
            error0 = 0.5*(Composite(tot,AlkStoi)-Alkfixed) ;
  else
            error0 = 0.5*(Composite(c,CarbAlkStoi)-Alkfixed) ;
```

```
  *I = IonicStrength(Species_Count,c,charge) ;

  if (( fabs(error0/Alkfixed) < tolerance) && (*residual < tolerance) && ((AlkOption < 2) || (fabs(1.0-(*I)/Ifixed)<0.01)))  // if the result is good enough already

   {
      *test1 = 0.0 ; *test2 = error0 ;
      return 1.0e-10 ;
   }

            // Solver loop (secant search)

   int count= 0 ; int rowbase = 0 ;
//
   while ((( fabs(error/totH) > tolerance) || (*residual > tolerance) || (count < 1)) ||
                ((AlkOption > 1) && (fabs(1.0-(*I)/Ifixed) > 0.01)) && (count < 40))
      {
                        if (count==0)
                        {
                                        if (error0 > tot[AdjustedComp[0]])
                                                error0 = 0.99*tot[AdjustedComp[0]] ;
                                        CO3tot1 = tot[AdjustedComp[0]] - error0 ;  // Adjust CO3= total concentration
                        }
                        else
                        {
                                        if (error0 == error)
                                                { newV = 0.5*(CO3tot0+CO3tot1); }
                                        else
                                                {newV = (CO3tot1*error0 - CO3tot0*error)/(error0-error) ;}
                                        if (newV > 3.0*CO3tot1)
                                                newV = CO3tot1*3.0 ;
                                        if (newV < CO3tot1/3.0)
                                                newV = CO3tot1/3.0 ;

                                        CO3tot0 = CO3tot1 ;
                                        if (newV > 2.0*CO3tot1 || newV < CO3tot1/2.0)
                                                CO3tot1 = newV*0.9+CO3tot0*0.1 ;
                                        else CO3tot1=newV ;
                        }
```

```
                adjust = 2*(CO3tot1-tot[AdjustedComp[0]]) - Herr ; // Adjustment to restore
charge balance
                tot[AdjustedComp[0]] = CO3tot1 ;
                error0 = error ;
                tot[AdjustedComp[1]]                                                    =
tot[AdjustedComp[1]]+adjust*0.5/ComponentCharge[AdjustedComp[1]] ;
                tot[AdjustedComp[2]]                                                    =
tot[AdjustedComp[2]]+adjust*0.5/ComponentCharge[AdjustedComp[2]] ;

                if (tot[AdjustedComp[1]]<0.0)  // if would make first ion conc -ve
                {
                        // transfer some adjustment to opposite charged ion
                        tot[AdjustedComp[2]] = tot[AdjustedComp[2]]

        +tot[AdjustedComp[1]]*ComponentCharge[AdjustedComp[1]]/ComponentCharge[AdjustedCo
mp[2]] ;
                        tot[AdjustedComp[1]] = 0.0 ;
                }
                if (tot[AdjustedComp[2]]<0.0) // if would make second ion conc -ve
                {
                        // transfer some adjustment to opposite charged ion
                        tot[AdjustedComp[1]] = tot[AdjustedComp[1]]

        +tot[AdjustedComp[2]]*ComponentCharge[AdjustedComp[2]]/ComponentCharge[AdjustedCo
mp[1]] ;
                        tot[AdjustedComp[2]] = 0.0 ;
                }

                Herr = TrySpeciation(logH, Adh, Component_Count, tot,
                         balance, BalanceCoef, BalanceMap, NonMaster,
          Species_Count, c, charge, k, gamma,
                         SpeciesID, Stoichiometry, SpeciesMap,
                         I, actwater, residual);

                tot[0] = tot[0]+Herr ;
                if (AlkOption==0||AlkOption==2)
                        error = 0.5*(Composite(tot,AlkStoi)-Alkfixed) ;
                else
                        error = 0.5*(Composite(c,CarbAlkStoi)-Alkfixed) ;
```

```
                    *I = IonicStrength(Species_Count,c,charge) ;

                    if (AlkOption > 1)  // adjusting ionic strength
                    {
                        adjust1 = 2.0*(Ifixed-(*I))
                            /((ComponentCharge[AdjustedComp[1]]-
ComponentCharge[AdjustedComp[2]])*ComponentCharge[AdjustedComp[1]]) ;
                        adjust2 = 2.0*(Ifixed-(*I))
                            /((ComponentCharge[AdjustedComp[2]]-
ComponentCharge[AdjustedComp[1]])*ComponentCharge[AdjustedComp[2]]) ;
                        if (adjust1 < -tot[AdjustedComp[1]])
                        {
                            adjust1 = -tot[AdjustedComp[1]] ;
                            adjust2 = -
adjust1*ComponentCharge[AdjustedComp[1]]/ComponentCharge[AdjustedComp[2]] ;
                        }
                        if (adjust2 < -tot[AdjustedComp[2]])
                        {
                            adjust2 = -tot[AdjustedComp[2]] ;
                            adjust1 = -
adjust2*ComponentCharge[AdjustedComp[2]]/ComponentCharge[AdjustedComp[1]] ;
                        }
                        tot[AdjustedComp[1]] = tot[AdjustedComp[1]]+adjust1 ;
                        tot[AdjustedComp[2]] = tot[AdjustedComp[2]]+adjust2 ;
                    }
                    count = count+1 ;
                }
/*                  // Final check on ion balance
                    error = 0.0 ;
                    for (ii=0 ; ii<Component_Count ; ii++)
                    {
              error = error+tot[ii]*ComponentCharge[ii] ;
              newtot[ii]=tot[ii] ;
            }
                    tot[AdjustedComp[1]] = tot[AdjustedComp[1]]-
0.5*error/ComponentCharge[AdjustedComp[1]] ;
                    tot[AdjustedComp[2]] = tot[AdjustedComp[2]]-
0.5*error/ComponentCharge[AdjustedComp[2]] ;
*/
     *pHeq = -log10(c[0]*gamma[0]) ;
```

```
            // Alkalinity calculation
            if ((AlkOption==0)||(AlkOption==2))
                  *Alkalinity = Composite(tot,AlkStoi) ;
            else
                  *Alkalinity = Composite(c,CarbAlkStoi) ;
      *test1 = double(count) ; *test2 = error ; // diagnostic values
      return 1.0 ;
   }
}
```

7.10 Initial Conditions for AD-FTRW2

Name	Value	Initial value	Unit
Category : DERIVED STATE			
M(Zmm)	0	0.01	g
M(Zhm)	0	500	g
M(Zfd)	0	0.01	g
M(Ze)	0	2900	g
M(Zam)	0	3100	g
M(Zad)	0	600	g
M(ZacVa)	0	2800	g
M(ZacPr)	0	5500	g
M(ZacHx)	0	300	g
M(ZacEt)	0	100	g
M(ZacBu)	0	1100	g
M(Va_t)	0	20.42636	g
M(Urea)	0	60	g
M(Sbp)	0	100	g
M(Pr_t)	0	59.26	g
M(PO4_t)	0	47.49	g
M(NH4_t)	0	108.23	g
M(Na_t)	0	11495	g
M(MeOH)	0	1.923	g
M(H_t)	0	6.23	g
M(Hx_t)	0	4.65	g
M(H2_t)	0	0	g
M(H2O)	1000000000	1000000	g
M(Fo_t)	0	0	g
M(EtOH)	0	1.84	g
M(CO3_t)	0	300	g
M(CO2)	0	0	g
M(Cl_t)	0	17148.62	g
M(CH4)	0	0	g
M(Bu_t)	0	44.05	g
M(Ac_t)	0	49.84	g