

Application of the IWA ADM1 model to simulate anaerobic digester dynamics using a concise set of practical measurements

U. Zaher*, J. Rodríguez**, A. Franco** and P. A. Vanrolleghem*

* Biomath Department of Applied Mathematics, Biometrics and Process Control, Ghent University, Coupure Links 653, B9000 Gent, Belgium (E-mail: Usama.Zaher@biomath.rug.ac.be, Peter.Vanrolleghem@rug.ac.be)

** Department of Chemical Engineering, University of Santiago de Compostela, Avd. das Ciencias, 15782, Santiago de Compostela, Spain. (E-mail: jorger@usc.es, afranco@usc.es)

Abstract This paper demonstrates how a complex model like the IWA Anaerobic Digestion Model no. 1 can be applied to gain more insight in the anaerobic process and particularly in the dynamics of the digester. The illustrated modelling approach avoids laborious measurements to characterise the influent according the extensive list of components defined in the model. It rather uses the model to make a better characterisation of the inflow. The model is applied to simulate a digester that was originally designed as a CSTR, i.e. with solids retention time equal to the hydraulic retention time. Because it is not practical to completely achieve this condition, an update to the model implementation is introduced to have a solids retention time that is proportional to the hydraulic retention time, i.e. with less efficient retention during overload conditions. The update is different from having a fixed difference between the two retention times as suggested for the standard model implementation for high rate reactors. The introduced approach shows better results for the illustrated application. Moreover, it proves that it can be more suited for high rate reactors operated under high flow dynamics.

Keywords ADM1; biomass washout; influent characterisation; practical measurements; solids retention

Introduction

Practical measurements in digester follow up are mainly based on available cost-effective methods that allow frequent measurements. Therefore, control strategies are developed on the basis of these measurements and on their on/off-line availability at reasonable price. Examples are pH, flow, gas pressure and gas flow which are practically available at anaerobic digesters and wastewater treatment plants in general (Vanrolleghem and Lee, 2002). Alkalinity and VFA measurements are available off-line and much efforts are invested to make them available on-line, e.g. by using titration (Di Pinto *et al.*, 1990; Hawkes *et al.*, 1993; Guwy *et al.*, 1994, Van Vooren *et al.*, 2001; Bouvier *et al.*, 2002; Feitkenhauer *et al.*, 2002), using gas / high pressure liquid chromatography (Zumbusch *et al.*, 1994; Banister and Pretorius, 1998; Pind *et al.*, 2001) and using intermediate infra red absorption (Steyer *et al.*, 2001).

Since, such measurements are more oriented towards control of the digester, they are more suitable for use with simple models that are developed in view of control systems, e.g. the two step mass balance model developed by (Bernard *et al.*, 2001). However, when more insight into the process dynamics is needed, models need to be adapted to cope with the complex characteristics of the wastewater and the way the biomass interacts with it. This means that an expansion of the

anaerobic digestion model is needed to involve more components that have a role in the process. Also a better characterisation of the influent wastewater must be performed. For example, the model developed by (Mosey, 1983) and the consequent expansion and enhancements in (Costello *et al.*, 1991; Romli, 1993; Ramsay, 1997; Batstone *et al.*, 2000^a; Batstone *et al.*, 2000^b) and finally the IWA ADM1 (Batstone *et al.*, 2002) is a reflection of their development.

This work is one of the first contributions to apply the IWA ADM1 model to simulate an experiment with important process dynamics treating a complex wastewater. Practical measurements, the model, information about the wastewater composition and knowledge about the industrial process producing the wastewater are used to expand the influent characteristics and define reactor behaviour.

Methods and materials

Anaerobic digestion model and its implementations

The model used in the present simulation is the IWA Anaerobic Digestion Model no. 1. The reader is referred to the complete description of the model in the IWA report (Batstone *et al.*, 2002). The present simulation uses a set of ADM1 parameters suggested in (Rosen and Jeppsson, 2002). Although this set of parameters was selected from the IWA ADM1 report for anaerobic digestion of secondary sludge, it is used for the present type of distillery wastewater. It is conceived that mainly the wastewater fraction parameters are the ones that should change with the change of wastewater source. As an initial set of parameters it gives good simulation results provided that influent is characterised in detail and, thus, influence of fraction parameters is reduced.

The simulation was performed using ADM1 implementations on three different simulation platforms, AQUASIM[®], WEST[®] and MATLAB SIMULINK[®]. The gas transfer is modelled on the first platform using a diffusive link between liquid and gas compartments and, therefore, the transfer is treated mathematically by partial differential equations and the gas flow is calculated for restricted flow through an orifice that is proportional to the piping resistance coefficient. In the second and third implementations, the gas components are modelled by differential equations in both liquid and gas phases and gas flow is estimated as a function of the gas transfer rates and the headspace pressure.

Reactor and wastewater composition

The reactor is a lab scale CSTR with a 2 liters liquid volume. It is equipped with pH and temperature probes, a stirrer to provide 200 r.p.m. and a condensation system in the gas outlet. A gas flow meter measures the gas production every 15 minutes. The temperature is fixed by a thermostatic jacket at 37 °C. The reactor is fed by charges of fresh wastewater in a semi-continuous mode. The reactor was inoculated with sludge produced at a pilot-scale plant treating dextrose with a specific methanogenic activity of 0.27 kg COD/m³·d, and its initial concentration in the reactor was 6 g VSS/l. The gas composition was measured with a thermal conductivity gas chromatography (HP 5890 SerieII), with helium as carrier gas.

Wastewater composition

The wastewater was collected from an alcoholic distillery plant and contained a high amount of TKN mainly in the form of protein. Average concentrations of the distillery wastewater are known for total COD, soluble COD, TOC, acetate, propionate, butyrate, TSS, VSS, protein, sugars, ammonia and sulphates. Due to the high concentration of wastewater, it is diluted before it is introduced to the reactor. This complex wastewater contains probably some unmeasured

compounds that could have slight toxic effects in some microbial populations. This fact appears as an extra source of uncertainties

Influent records

Influent flow and pH were recorded on-line. TOC, soluble COD, total volatile fatty acids (VFA), total alkalinity (TA) and partial alkalinity (PA) were analysed off-line and recorded on daily basis.

Digester/effluent records

pH, gas flow and gas composition (%CO₂ and %CH₄) were measured on-line. Specific VFA gas chromatography analysis, TA and PA, total organic carbon and COD were measured in the digester on daily basis.

Influent characterisation

In a first step, information about the wastewater composition was used to extend the practical set of measurements to the IWA ADM1 influent characteristics. The IWA ADM1 has a detailed structure that presents most of the anaerobic digestion process path-ways and possible inhibitions. Therefore, in a second step, the certainty encapsulated in the detailed structure of the model is used to resolve uncertainties encountered during influent characterisation.

First step in extending the practical measurements

Based on the wastewater average composition, it is concluded that the main part is in the form of soluble COD (CODs). A dilution factor (D) is estimated at every measuring point as the ratio of CODs average composition to the CODs measurement.

$$COD_{S_{in}} \cdot (WW + W) = COD_{S_{composition}} \cdot WW$$

$$D = \frac{(WW + W)}{WW} = \frac{COD_{S_{composition}}}{COD_{S_{in}}}$$

where:

WW is assumed average wastewater produced by the plant

W is assumed water added for dilution

Then this factor is used to estimate unmeasured components. For example influent inorganic

nitrogen S_{IN_m} is in the form of ammonia: $S_{IN_m} = \frac{S_{NH_4^+-N}}{14 \cdot D}$

Similarly other unmeasured components are estimated from the wastewater composition. Also information about the type of waste and the manufacturing process helps in the determination of molecular weights and COD contents that are needed to convert measurement units to the model COD units. Influent soluble sugar, S_{su_m} , is estimated from the sugar composition assuming that it is mainly monosaccharides. Influent composite particulate, X_{C_m} , are estimated from the total suspended solids, TSS, composition assuming that it has the same composition of biomass since X_{C_m} is used within the model as a sink for decaying biomass. Influent inert particulate are estimated as the difference of TSS and volatile suspended solids, VSS. Particulate protein was estimated from the wastewater composition and it was assumed to have an equal molecular weight and COD content since its molecular formula is not known. This assumption will affect the

predictions of the amino acids and their conversion to different volatile fatty acids, inorganic nitrogen, inorganic carbon and hydrogen gas in the reactor.

VFA specific components were estimated from the daily measurement of the total VFA concentration and fractions to acetate, propionate and butyrate according are estimated according to their average proportions in the wastewater. Influent soluble COD measurement was found to be higher than the sum of the COD of the estimated influent sugar and VFAs. This extra COD was redistributed using the ADM1 model in the next step.

Estimate of inorganic carbon

If anions in the influent are mainly due to bicarbonate and VFA and the influent pH is in the optimum range of 6 to 8, the estimate of the inorganic carbon is straight-forward from the practical measurement of TA. TA is determined by the volume of acid added to a sample till the pH reaches 4.3 and will be equivalent to the total concentration of cations (Bernard *et al.*, 2001). The total VFA concentration can be estimated, e.g. by recording the volume of acid added to the titrated sample at pH 5.75 and then the total acid till pH 4.3 (Ripley *et al.*, 1986). In such case, the inorganic carbon will be mainly due to bicarbonate (Van Haandel and Lettinga, 1994) and it will equal the total cation concentration minus VFA concentration.

In the present case study anions other than bicarbonate and dissociated VFA are expected in the influent. We assume that anions (San) of strong acids eg. (Cl⁻) will be in chemical equilibrium with ammonium NH₄⁺ and thus will equal its concentration. Influent anions of other acids (in oxidised form e.g. SO₄²⁻) will influence the charge balance with the influent cation. In the digester, such anions are not considered any further in the charge balance since they are expected to be reduced due to acidification while evaluated cations remain and influence the charge balance.

Total alkalinity will not correspond to VFAs and bicarbonate but also to the other ions (Lahav *et al.*, 2002). Since the additional ions in the influent are not measured in the influent, IWA ADM1 itself is used to resolve this uncertainty. First, the inorganic carbon is estimated from PA. PA is the amount of acid added to a sample till it reaches pH 5.75. In this narrow range most of the influence of the different buffering system is avoided. However, VFA have a considerable influence to the PA measurement in this range (Lahav and Loewenthal, 2000). Total VFA is measured in the influent and thus a proportion of VFA deducted from the partial alkalinity value to get an initial estimate of the inorganic carbon (bicarbonate).

Use of the ADM1 to better characterise the influent composition

Better characterisation is needed with two objectives in mind. The ADM1 model will be used to enhance the initial estimate of cations and distribute the extra COD detected to model components. These two objectives are met by defining parameters (multipliers / fractions) to the concerned influent components and estimate them by fitting the digester COD, acetate, propionate, pH as follows.

Enhancing the initial estimate of influent cations

pH is measured in the influent and thus an initial estimate of the cations is obtained as the sum of bicarbonate and dissociated VFA (as acetate):

$$S_{Cat-initial} = \frac{IC \cdot Ka_{HCO_3}}{Ka_{HCO_3} + \{H^+\}} + \frac{VFA \cdot Ka_{acetate}}{Ka_{acetate} + \{H^+\}} \quad (1)$$

A parameter P_{cat} is added to the model according equation 2.

$$\text{Influent } S_{\text{cation}} = P_{\text{cat}} * S_{\text{cat-initial}} + \text{external cation pulses} \quad (2)$$

External cation pulses are recorded base additions to adjust the influent pH. With a sensitivity analysis it was shown that the IWA ADM1 is very sensitive to this added parameter. The parameter P_{cat} is then estimated by fitting the most sensitive and measured state variables. The parameter P_{cat} is used to scale the estimated cation concentration to compensate for the extra ions expected in the influent. Provided that the wastewater is from the same origin, the cation concentration will vary according to the dynamics of the other influent concentrations. Therefore, different values $P_{cat,i}$ can be estimated in equation 3 according to the major changes observed in the influent concentrations, e.g. COD.

$$P_{cat_{0 \rightarrow t}} = \begin{matrix} \mathbf{P} \\ \mathbf{cat} \end{matrix} (1)_{0 \rightarrow t_1}, P_{cat}(2)_{t_1 \rightarrow t_2}, \dots, P_{cat}(n)_{t_{n-1} \rightarrow t} \quad \mathbf{S} \quad (3)$$

In the present case study P_{cat} was estimated in two intervals from day 0 to 100 and from day 100 till the end of the experiment. Indeed the influent COD concentration was reduced by 50% after 100 days.

Distribute the extra COD detected to model components

The influent wastewater contains protein. Amino acids are expected from hydrolysis of proteins and therefore their concentration has to be estimated. The wastewater is produced from an industrial process that depends on the fermentation of grains (e.g. barley). Grain contains some oil content that will not be processed during the industrial processes. Oil is expected to hydrolyse to long chain fatty acids LCFA in the wastewater and therefore needs to be estimated as well. Extra COD can be attributed to fatty acids and amino acids by estimating two fraction parameters, equations 4, 5. To allow more degrees of freedom and check the assumption, two fraction parameters are added in equation (6 and 7) to estimate extra acetate and propionate since they are already high in the influent. The sum of these fraction parameters is expected to be less than 1 since some of the extra COD is expected to be inert soluble or particulate matter escaped the filtration done before performing the COD measurement. This fraction is determined by equation 8.

$$S_{aa_{in}} = f_{aa} \cdot COD_{extra} \quad (4)$$

$$S_{fa_{in}} = f_{fa} \cdot COD_{extra} \quad (5)$$

$$S_{ac_{in_adjusted}} = S_{ac_{in_estimated}} + f_{ac} \cdot COD_{extra} \quad (6)$$

$$S_{pro_{in_adjusted}} = S_{pro_{in_estimated}} + f_{pro} \cdot COD_{extra} \quad (7)$$

$$S_{inert/escaped_particulate} = \mathbf{d} - f_{aa} - f_{fa} - f_{ac} - f_{pro} \cdot \mathbf{i} \cdot COD_{extra} \quad (8)$$

Parameter estimation resulted in a small value of f_{ac} and f_{pro} that can be ignored. Therefore, confidence has been increased that extra measured COD is mainly due to fatty acids and amino acids, which can be expected in the influent.

Detection of changes in particulate dynamics

The IWA ADM1 model will be used to detect whether the observed process dynamics were either due to wash out of biomass or due to higher retention. However, minor update had to be implemented to the model. For a perfect CSTR the rate of change of the particulate concentration is calculated according equation (9). Originally, it is recommended in the model report (Batstone et al., 2002) that for the description of a higher solids residence time (SRT) in a biofilm or a high-rate reactor, the retention time can be extended by implementing an extra residence time (equation 10) above the hydraulic retention time in the second term (particulate mass flow out) of the particulate concentration mass balance.

$$\frac{dX_{liq,i}}{dt} = \frac{qX_{in,i}}{V_{liq}} - \frac{qX_{liq,i}}{V_{liq}} + \sum_{j=1-19} \rho_j v_{i,j} \quad (9)$$

$$\frac{dX_{liq,i}}{dt} = \frac{qX_{in,i}}{V_{liq}} - \frac{X_{liq,i}}{t_{res,X} + V_{liq}/q} + \sum_{j=1-19} \rho_j v_{i,j} \quad (10)$$

and in terms of flux rate of change equation 10 is written :

$$\frac{V_{liq} \cdot dX_{liq,i}}{dt} = qX_{in,i} - \frac{V_{liq} \cdot X_{liq,i}}{t_{res,X} + V_{liq}/q} + V_{liq} \sum_{j=1-19} \rho_j v_{i,j} \quad (11)$$

The second term represents the particulate mass flow out $J_{X_{out}}$:

$$J_{X_{out}} = \frac{V_{liq} \cdot X_{liq,i}}{t_{res,X} + V_{liq}/q} = \frac{V_{liq} \cdot X_{liq,i}}{SRT} \quad (12)$$

In the present implementation, $J_{X_{out}}$ is calculated in a different way, i.e. we apply a factor :

$$J_{X_{out}} = f_{X_{out}} \cdot q \cdot X_{liq,i} \quad (13)$$

Equating equation 12 and 13 : $f_{X_{out}} = \frac{V_{liq}/q}{SRT} = \frac{HRT}{SRT}$

Equation 14 defines a proportional relation between HRT and SRT . During hydraulic over-loads applied to high rate reactors, the HRT will drop and the SRT will drop proportionally rather than having a fixed difference. In terms of the solid retention time, reactors theoretically vary from a completely stirred tank reactor CSTR to perfectly fixed bed reactor PFBR. For a CSTR $f_{X_{out}}$ equals one and for a PFBR $f_{X_{out}}$ is 0. In the original implementation the corresponding values of $t_{res,X}$

range from 0 to infinity respectively. For estimation of f_{xout} , minimum and maximum boundaries can be easily assigned that makes it easier to estimate.

Moreover, values > 1 can be assigned to f_{xout} to simulate biomass washout events (e.g. more biomass flocs in the effluent of a CSTR due to a defect in mixing or floating of the sludge bed in a UASB). In the present case study washout is simulated this way between day 55 and day 85. This effect also can be simulated by assigning $t_{res,X}$ a negative value but its magnitude should be assigned carefully. If $t_{res,X}$ is assigned a value higher than the HRT, the result will be, according equation 11, as if biomass was added to the reactor and not washed out. This event is likely to happen when HRT is very small during hydraulic shocks.

Results and discussion

“All anaerobic processes simulated by the ADM1, both biological and physico-chemical, except perhaps disintegration and hydrolysis, are affected by either competition for substrate, inhibition by H_2S , or the acid-base reactions and gas–liquid transfer of H_2S . Because of its complexity, the sulfate reduction system was not included in the ADM1. The ADM1 is therefore incapable of modelling systems with low to medium amounts of sulphide (>0.002 M influent SO_x).” (Batstone et al., 2002). In the presented experiment influent contains low concentration of sulphate that varies from 0.001 to 0.002 mol/l. The ADM1 simulated the experiment dynamics nicely. Influent sulphates increased up to 0.003 during the high organic load applied in the last 7 days of the experiment. At these low sulphate concentrations, a careful estimate of the cations is necessary to compensate for the presence of sulphate since the major influence will be due to its effect on the acid base reactions. Sulphates will be reduced to S^{2-} which due to acidification in the reactor will be reduced to $HS^- \leftrightarrow H_2S$ (with a lower equivalent concentration compared to the original sulphates). The equilibrium $HS^- \leftrightarrow H_2S$ will be determined by the reactor pH. Influent cations that were associated with sulphates will remain influencing the charge balance and therefore the calculations of the pH in the reactor.

It can be seen from figures 1 and 2 that the simulation results from the three IWA ADM1 implementations on different simulation platforms are giving the same results. The dynamics to the digester are caused mainly by three perturbations and the process crash at the end of the experiment. Biomass washout from day 55 to day 85 produced the first perturbation accompanied by an increase of the hydraulic and organic over-load. The second is affected by two consequent doses of bicarbonate at day 68 and day 70. The third perturbation is due to a sudden increase of the OLR (shock load) during the period 117 to 125 days. From day 165 till the end of the experiment, two step increases of the OLR stopped the process.

Liquid phase simulation results

Figure 1 shows the liquid phase results. The first and third perturbations lead to two peaks in acetate, propionate and soluble COD from day 60 to day 108 and from day 118 to day 137. Estimation of the LCFA from the extra COD in the influent produced a better fit to the first acetate peak. Indeed, according the model stoichiometry, the uptake of LCFA yields VFA in the form of acetate only. Similarly, the estimation of the influent amino acids enhanced the fit during the second peak and produced the corresponding peak in butyrate (similarly in valerate, not shown). According the model stoichiometry, the uptake of amino acids produces all VFAs and, especially, valerate is only produced through the uptake of amino acids. Moreover, CODs is calculated by summing all soluble components considered in the model (e.g. sugar, inerts, VFAs,...etc.) and results are showing a good fit to the measurements. This confirms the validity of the extra CODs distribution

in the influent. The acetate simulation results are slightly higher during the period 140 to 160 this could be related to uptake by sulphate reducing bacteria which is not accounted for in the model. A corresponding effect will be shown in the simulation results of the gas phase.

Alkalinity

Figure 1 shows the alkalinity results. The TA simulation results are calculate by summing the bicarbonate and all VFA ionised forms (scaled to meq/l). It shows a nice fit to the TA measurements. Thus, the TA in the reactor is mainly due to bicarbonate and VFA in contrast to the situation in the influent that is influenced by other ions. The PA simulation is plotted as the meq/l of the simulated bicarbonate.

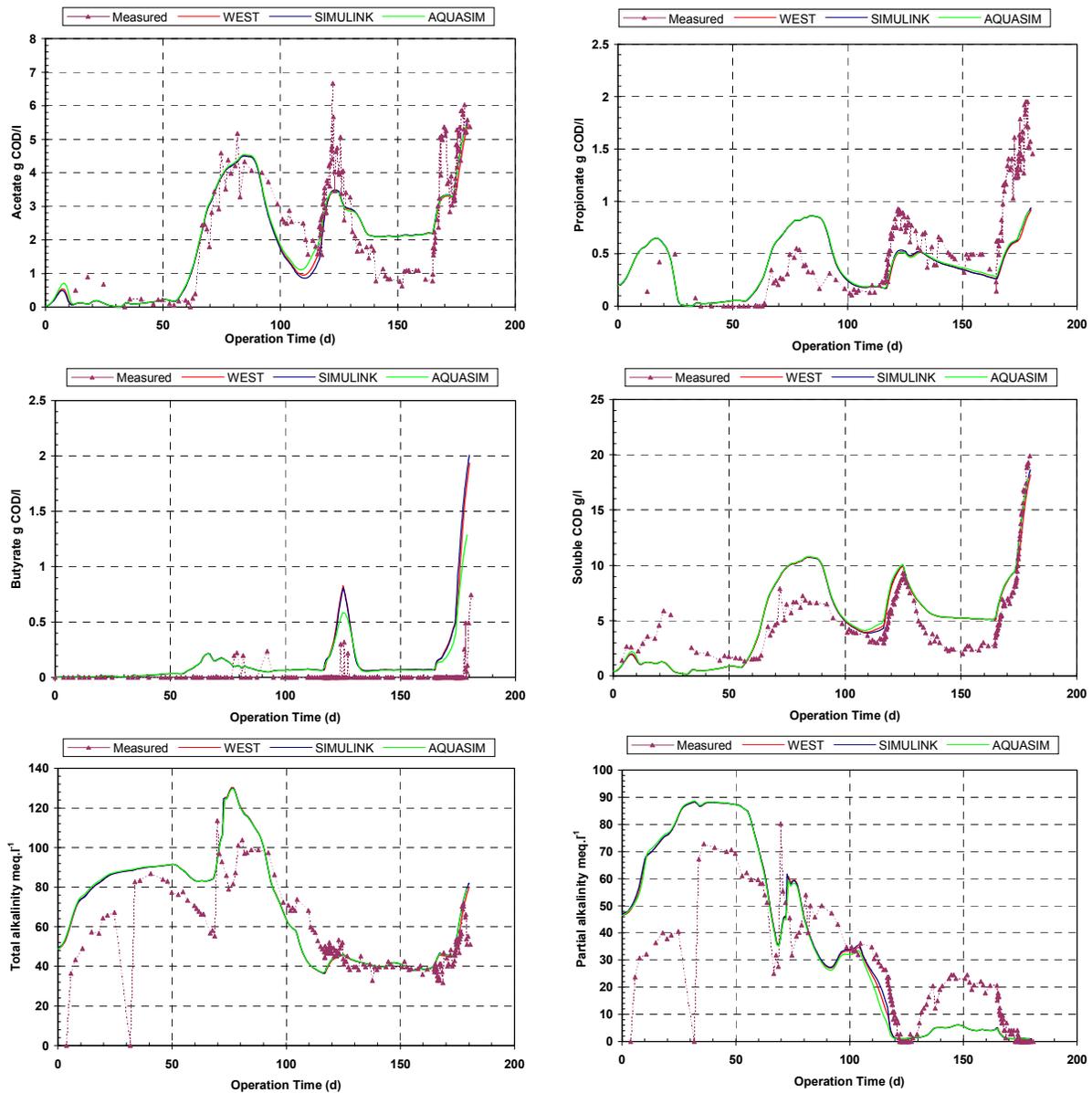


Figure 1 Liquid phase results

It corresponds with the dynamics of PA measurements, but the simulation tends to underestimate the measurements when the VFA concentrations increase during the first and third perturbations. The PA measurements are indeed slightly influenced by the presence of VFA. Therefore reduction in proportion to the VFA concentration was required during the estimation of the influent inorganic carbon (refer to influent characterisation). During the period from 140 days to 160 days, a larger underestimation of PA is shown. In addition to the VFA influence, HS^- buffer at a pKa of 7.05 will influence the PA measurement due to the expected sulphate reduction activity. This effect is not shown in the total alkalinity results for two reasons. First, the acetate is overestimated in the same period. Second, through the charge balance, the better estimate of the influent cations conceals the effect of sulphate reduction (change of equivalent concentration: $\text{SO}_4^{2-} \rightarrow \text{S}^{2-} \rightarrow \text{HS}^- \leftrightarrow \text{H}_2\text{S}$).

Gas phase and pH simulation results

pH dynamics in the reactor

It is shown in Figure 2 that the pH is almost fitting the measurements. To achieve this the influent cations concentration had to be adjusted as mentioned above. This leads to a better estimation of the inhibition factors and therefore a better estimation of the other variables. In the beginning of the experiment, however, the simulated pH is higher than the measurement but it adapts to the measurement after 40 days. This is similar for the alkalinity results. This is mainly due to the initial conditions. Better estimates of the initial values can be obtained by fitting the first 40 to 60 days of measurements of VFA. However, in this experiment it was difficult since the VFA measurements were less frequent during this start up period.

Gas phase dynamics are shown in figure 2. The % CH_4 is calculated from the ratio of the simulated methane partial pressure to the simulated total pressure including adjustment for the water vapour pressure. The % CO_2 is calculated. Although calculation procedure of gas transfer and flow applied in the AQUASIM implementation is different than in the SIMULINK and WEST implementations, the simulation results are almost the same. Good results are obtained during the first perturbation. In second perturbation immediate stripping of the added bicarbonate in the form of CO_2 occurred and the result was reflected in the percentage of methane and the total gas flow. However, the measured gas composition and flow are lower and thus a lower transfer rate should be considered. Another interpretation is a limitation of the gas sensor to measure such large difference in the gas composition. Further study is clearly needed.

After the start of the third perturbation a worse fit to the measurements is shown. These overloads are accompanied by a drop in the pH from 6 to 5 and thus inhibition of all biological reactions. An increase is shown in the hydrogen concentration leading to inhibition of acetogenesis. During the third perturbation and during the extreme overload at the end of the experiment, the simulation results show lower methane and higher CO_2 concentrations while there is a decrease in the simulated gas flow. These results could be attributed to inhibition phenomena but it is more likely due to the production of other gases that influenced the gas measurement. During overload, hydrogen sulphide is produced in addition to the produced hydrogen. Higher concentrations of sulphates are applied to the reactor (>0.002 mole/l). Hydrogen sulphide and hydrogen were not considered in the measurement method of the gas composition while it will be accounted for in the gas flow measurement. This indeed can contribute to the difference.

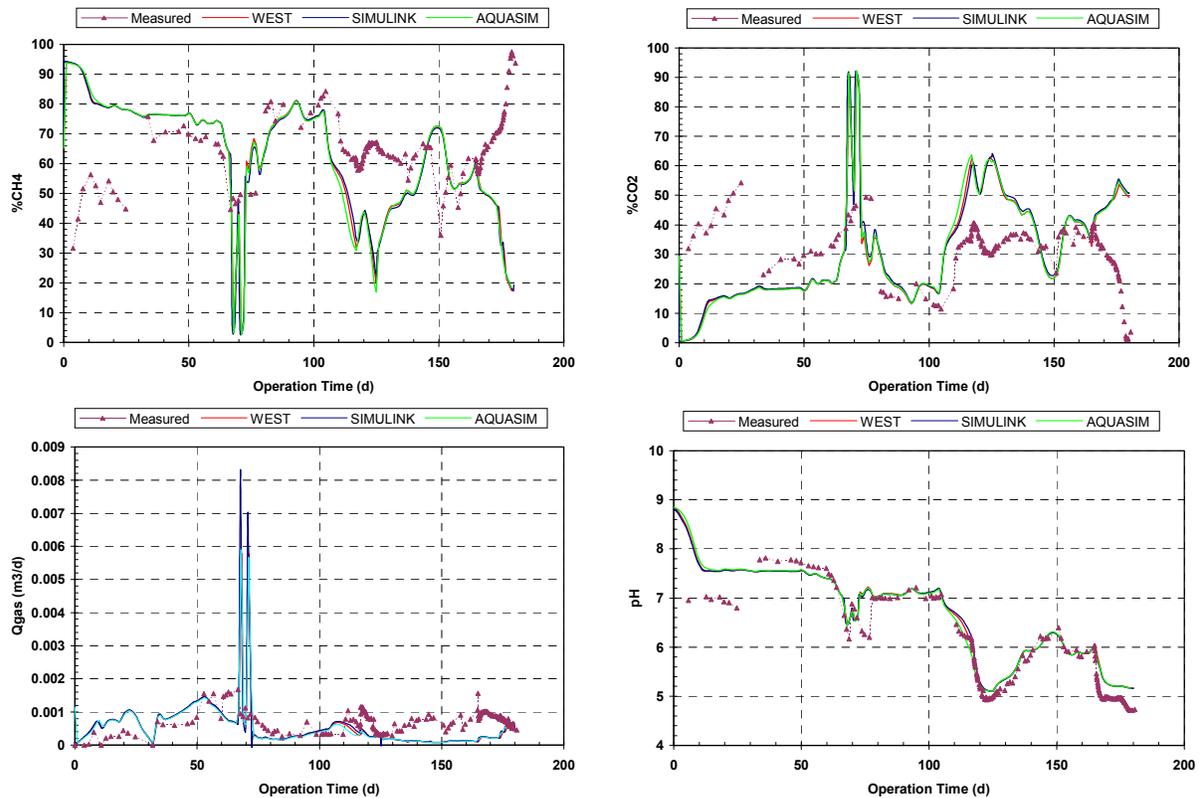


Figure 2 pH and gas phase dynamics

Conclusions

Information about the wastewater composition and knowledge of the upstream industrial processes was used successfully to extend the concise set of practical measurement and achieve detailed characterisation of the influent wastewater. This detailed characterisation of the influent produced good simulation results using a default set of parameters that was selected for different type of waste. The detailed structure of the IWA ADM1 model helped to distribute COD measurement to expected components leading to better simulation results. Also, the ADM1 model was used to enhance the estimation of the influent cation concentration. This was necessary to achieve good simulation results in the presence of unmeasured anions and low concentrations of sulphate. The increase of sulphate concentration in the influent to levels higher than 0.002 M and drop of the pH caused a disturbance to the gas measurements that may be due to hydrogen sulphide production. A model extension might be necessary to describe this phenomenon.

A change was made to the method to describe the SRT in proportion to the HRT. It uses a parameter with known bound for high rate anaerobic reactors, therefore leading to a better parameter identifiability. Moreover, the new introduced parameter can be used to detect/estimate washout of biomass from the reactor.

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