The role of CO_2 liquid-gas exchange in pH prediction for anaerobic digestion modelling.

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Abstract
pH plays a major role in the operational stability of anaerobic digesters, so accurate prediction of pH is a key goal of anaerobic digestion process models. Modelling of abiotic aqueous chemistry is a well-established discipline, but most current wastewater treatment models have neglected its techniques in comparison to the sophistication applied to biological reactions. Two case studies of applications of integrated biochemical/physico-chemical anaerobic digestion models are presented which illustrate the key role of CO_2 liquid-gas exchange in determining the system pH.

Keywords
Anaerobic Digestion Modelling, ionic speciation, pH prediction, CO_2 liquid-gas exchange.

INTRODUCTION

A recent initiative of the IWA has focussed on establishing a comprehensive physico-chemical modelling framework for biochemical process models to address issues such as more rigorous and accurate pH prediction (Batstone et al., 2012). Anaerobic digestion (AD) exhibits a particularly intricate interaction between biochemical and physico-chemical processes, since the biological reactions produce and consume weak acid/base components, and are significantly affected by the resulting changes in their concentrations. The UCTADM2 anaerobic digestion model (Brouckaert et al., 2010) was specifically developed to address these issues. It combines representation of organic components by molecular formula of the form $C_xH_yO_zN_aP_b$, reaction stoichiometry which conforms to C, H, O, N and P balances, and detailed equilibrium speciation of inorganic ionic components.

Two case studies, applying variants of UCTADM2 to data from laboratory digesters have highlighted the importance of CO_2 liquid transfer in determining the system pH. The first involved adding pure ethanol as substrate to an digester containing sludge taken from a brewery effluent digester. The second involved digestion of a synthetic mixture of organic acids and alcohols representing Fischer-Tropsch Reaction Water (FTRW), a high strength wastewater produced by Fischer-Tropsch gas-to-liquid hydrocarbon reactors. It has an organic load of 18000 mgCOD/L and is highly acidic with pH 3.8. In both cases, the pure components used to make up the feeds meant that their elemental makeups were precisely known, which avoided the some of the uncertainties usually associated with AD of municipal streams.

MATERIALS AND METHODS

Modelling

Modelling of an anaerobic system can be divided into three main categories: the biological reactions, the physico-chemical processes, and the reactor unit model. In this instance, the UCT ADM2 model was used to describe the biological and physico-chemical system. (Ikumi, 2011) UCT ADM2 uses differential equations to describe the kinetics of the biological reactions, but describes aqueous ionic reactions using an algebraic equilibrium speciation model (Brouckaert et al., 2010). The gas phase model assumes that the methane is insoluble: thus all methane is immediately transferred to the headspace. The solubility of carbon dioxide is significant, therefore its transfer to the gas phase was modelled using non-equilibrium liquid-gas transfer (Batstone et al., 2002).

The ethanol degradation model used the Ikumi (2011) formulation, modified by adding ethanol as a component, plus a micro-organism group to mediate its degradation.

For the FTRW model, a thorough rewrite was necessary to accommodate the very different feed compostion, although the conceptual basis was exactly the same. The set of components were:

Organic anions: formate, acetate,proprionate,valerate,butyrate and hexanoate;

Other organic substrates: methanol, ethanol, H_2 and urea

Inorganic anions: $CO_3^{=}$, Cl^-

Cations: H^+, NH_4^+, Na^+

Biomass: 9 separate populations, each degrading one of the substrates (apart from urea which was dosed to provide N for biomass growth).

Gases: CO_2, CH_4 and water vapour.

The anions and cations constituted the component set for the ionic speciation sub-model.

WEST (www.mikebydhi.com) was used as the modelling environment for these models.

Experimental

The experimental data for the FTRW investigation was taken from Van Zyl (2008). The experimental setup consisted of a 23 litre Anaerobic Membrane Bioreactor (AnMBR) with Kubota® flat panel ultrafiltration membranes (0.45µm). Biogas from the headspace was re-circulated to sparge the membrane surfaces, and so reduce fouling. Excess biogas was vented through a cumulative gas meter to monitor biogas production. Batches of feed was made up of C_2 to C_6 organic acids, ethanol and methanol and was conditioned with nutrients and some $NaHCO_3$ to provide alkalinity (~800 $mgCaCO_3/L$) to render it amenable to anaerobic digestion and to raise the pH to 4.5, similar to actual FTRW. Sodium hydroxide was dosed to control the reactor pH. The total experimental operation covered 685 days. A period of 30 days of steady and stable operation was selected for the pH and alkalinity investigation presented here. No model parameters were adjusted to fit this set of data. Biological reaction parameters had been calibrated separately using other sections of the experimental data. The pH prediction model used only established literature parameter values without any adjustment. Although the CO_2 mass transfer coefficient was potentially a calibration parameter, the re-circulation of the biogas (in order to prevent fouling of the membrane surfaces) resulted in the system being very close to vapour-liquid equilibrium.

Ethanol degradation was carried out in a 6.4 l batch reactor, containing 4.4 l of sludge (27 gVSS/l) taken from a brewery effluent digester. For the ethanol degradation test, 5ml of pure ethanol was added without additional alkalinity or nutrients. Gas flow rate was measured by an Aalborg mass flowmeter; temperature and pH were measured every minute.

RESULTS AND DISCUSSION

FTRW digestion

Figures 1 and 2 compare experimental pH and alkalinity data with prediction from 3 versions of the model in which main difference was in the characterisation of the feed to the reactor. In model A (dotted line) the feed was simply the combination of all the components that were added experimentally, including the $NaHCO_3$ and NaOH as dosed. The fluctuations in the model reflect the daily variations in NaOH dosage. In seeking an explanation of the systematically low pH prediction, it was realised that the model did not account for water vapour in the reactor head space, so that, in particular, the partially pressure of CO_2 was slightly too high. Including this correction caused a slight improvement (model prediction B), but not enough to match the measured pH values. Then it was realised that, when $NaHCO_3$ was added while making up the feed batches, the

low pH would cause evolution of CO_2, which would therefore not be fed to the digester. Since the experimental programme had been completed some years previously, the amount of CO_2 lost could not be measured, but was estimated by modelling the feed composition in equilibrium with the atmospheric partial pressure of CO_2 (0.00032 bar). Applying this correction resulted in a satisfactory correspondence with the measured pH (prediction C). The alkalinity predictions were only slightly affected by these corrections (Figure 2).

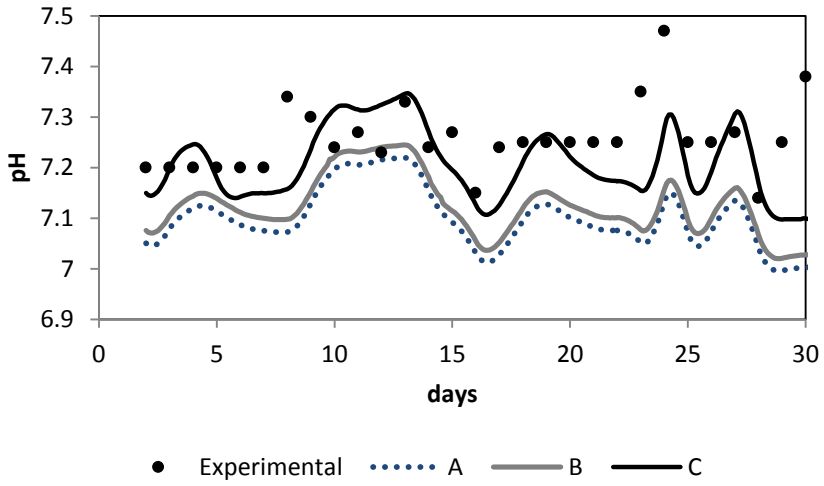

Figure 1: Comparison of pH measurements with 3 FTRW digestion model predictions.

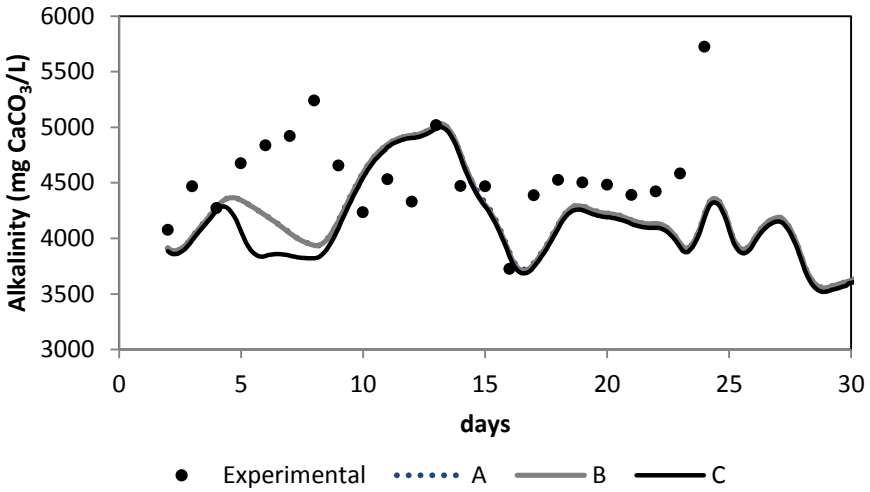

Figure 2: Comparison of alkalinity measurements with 3 FTRW digestion model predictions.

Ethanol degradation

The purpose of the laboratory batch reactor was to provide data for estimating parameters for model-based control of anaerobic co-digestion of municipal and industrial streams. A parameter identifiablity analysis of the ethanol degradation experiment had indicated that the kinetic parameters that could be reliably estimated from the batch ethanol digestion experiment were a) one of either biomass concentration, maximum growth rate or saturation coefficient for each of the main biochemical reactions (ethanol degradation, acetoclastic methanogenesis and hydrogenotrophic methanogenesis; and b) the mass transfer coefficient for CO_2 transfer from the liquid to the headspace gas. Figure 3 shows the results of fitting these parameters to an experimental run: the kinetic parameters chosen for the regression were the biomass concentrations – literature values

were used for the maximum growth rates and saturation coefficients.

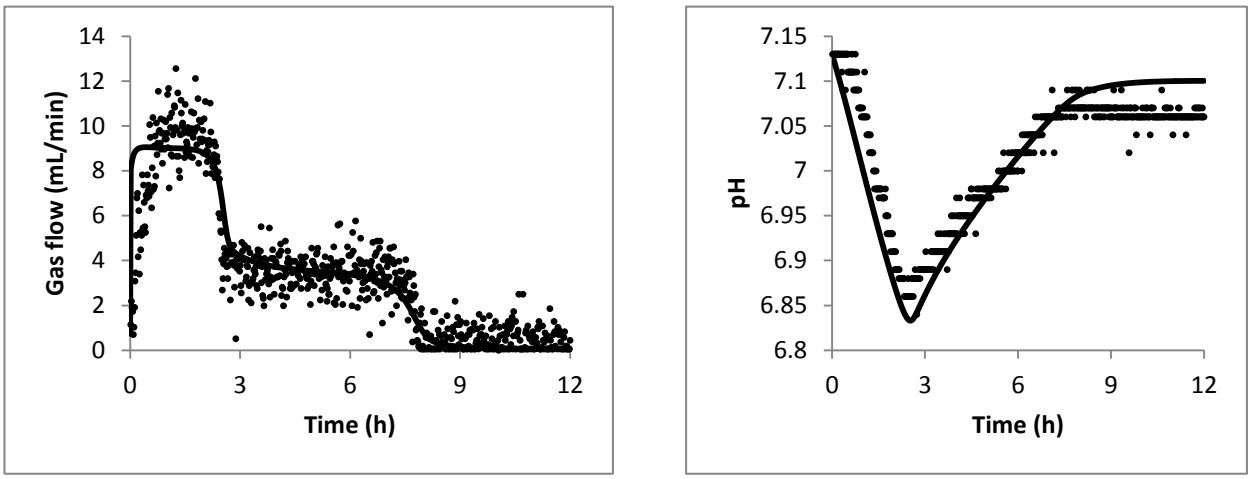

Figure 3: Fit of model to experimental data for ethanol degradation in an anaerobic batch reactor

However, due to an experimental oversight, there was considerable uncertainty in the value of the alkalinity, in particular the carbonate alkalinity, of the sludge that was charged to the reactor before the ethanol was dosed. An analysis of the sensitivity of the model to initial total carbonate concentration was carried out by increasing the nominal alkalinity of the sludge from 2067 to 2247 mg $CaCO_3$/L (10%) and re-running the parameter regression (Table 1). Whereas the biological kinetic parameters were little changed, the CO_2 mass transfer coefficient was reduced by almost 40%, principally to fit the pH data.

Table 1: Sensitivity of parameter regression to total alkalinity.

Parameters	Original values	Increased alkalinity values
Mass of ethanol (g)	2.60	2.63
Acetoclastic Methanogens (g/L)	0.90	0.95
Hydrogenotrophic Methanogens (g/L)	1.52	1.58
Ethanol Degraders (g/L)	4.91	4.96
Mass Transfer Coefficient for CO_2 (1/d)	0.23	0.14

CONCLUSION

Rigorous ionic speciation provides anaerobic digestion models with increased accuracy for pH prediction, but requires additional attention to detail in the physico-chemical modelling. In particular these case studies point to the importance of the representation of CO_2 exchange processes.

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