Disintegration and hydrolysis kinetics modelling for ADM1 application to codigestion: lab-scale model calibration with fruit and vegetable waste

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Abstract
A methodology to estimate kinetic parameters and validate an ADM1-based anaerobic codigestion model is presented. Kinetic parameters as well as readily and slowly biodegradable fractions, and non-biodegradable fractions were calibrated from batch reactor experiments of fruit and vegetable wastes. Calibrated parameters from batches were used to validate the model for an anaerobic codigestion process, treating simultaneously 5 fruit and vegetable wastes (lettuce, potato, apple, carrot and banana) in a continuous operation. The experiment was carried out in a CSTR reactor (10 L capacity) for 15 weeks at organic loading rate (OLR) ranging between 2.0 and 4.7 g VS/kg·d. The model (built in MATLAB/SIMULINK) fit to a large extent the experimental results. The methodology to estimate parameters and the anaerobic codigestion model for particulate substrates were validated.

Keywords
Anaerobic codigestion, characterisation, kinetics, modelling, ADM1

INTRODUCTION

In 2002, the IWA task group for mathematical modelling developed *Anaerobic Digestion Model No.1*, ADM1, (Batstone et al., 2002) that it serves as a reference for on-going models on anaerobic digestion (AD) and codigestion (AcoD). The majority of papers dealing with AcoD modelling appeared in 2008-2009 (Fezzani and Ben Cheikh, 2008; Zaher et al., 2009). And research on AcoD modelling has recently increased (Mata-Álvarez et al., 2011).

Here, a methodology to obtain and calibrate hydrolysis kinetic parameters for an ADM1-based AcoD model (Garcia-Gen et al., 2013) from batch reactor assays of particulate substrates (fruit and vegetable wastes, FVW) is presented. An estimation of readily and slowly biodegradable fractions, as well as the non-biodegradable fraction of each substrate from batch reactor assays is included.

The model is validated by simulation of the codigestion of a blend of five FVW in a continuous lab-scale operation, using the parameters obtained from batch reactor assays of each individual substrate.

MATERIALS AND METHODS

Batch assays methodology for FVW is described elsewhere (Torrijos et al., 2013). Batch reactors experiments where preferred to BMP assays for two main reasons: (i) carrying out several successive batches makes it possible to work with biomass acclimatized to the substrate (no lag phase), (ii) the S0/X0 ratio is low and close to that of industrial reactors (0,08 instead of 0,5-1 in BMP. A continuous operation treating 5 FVW at mesophilic conditions (lettuce, apple, potato, banana and carrot) was tested with the model and compared with experimental results treating these substrates for 15 weeks at 2.0 g VS/kg·d (first 10 weeks), 3.5 g VS/kg·d on week 12, 3.8 g VS/kg on weeks 13 and 14, and 4.7 g VS/kg·d (week 15) in a 10 kg CSTR reactor at HRT of 80, 45, 45, and 36 days, respectively (reactor fed 5 times a week). And ADM1-based AcoD model was used to simulate the operation from weeks 2 to 15. The model includes a general methodology to incorporate particulate substrates into ADM1 to extend the model for AcoD general application.

RESULTS AND DISCUSSION

A methodology to calculate kinetic parameters of disintegration and hydrolysis, readily and slowly biodegradable fractions and non-biodegradable fractions from batch experiment of particulate substrates was developed. These parameters were calibrated in an ADM1-based AcoD model.

Disintegration reaction. ADM1-AcoD model

The anaerobic digestion of solid wastes often implies disintegration/hydrolysis as the rate limiting step of the overall kinetic. Batch assays of solid wastes typically show however two different stages for the overall kinetics: in the initial steps, the overall rate is fast (as readily biodegradable organic matter is being converted to biogas) and after a certain time, the rate slows down (as all readily organic matter has been converted to biogas, and only slowly biodegradable matter remained). Based on this observation, the particulate complex substrates (defined and calculated as the linear combination of protein, lipid, carbohydrate and non-biodegradable fibre contents obtained from characterisation) can be expressed as the addition of two fractions:

$$Complex\,substrate = X_{CS,\ READILY} + X_{CS,\ SLOWLY} = f_{XR} \cdot X_{CS} + (1 - f_{XR}) \cdot X_{CS}\ .$$

ere f_{XR} $\boldsymbol{f_{XR}}$ is the readily fraction of the particulate substrate X_{CS}

A new disintegration kinetic mechanism for particulate substrates is proposed in the ADM1-based AcoD model. The disintegration reaction is split into two fractions, disintegration of readily- and disintegration of the slowly-biodegradable fraction respectively (both as first order kinetics).

$$-\frac{dX_{CS}}{dt} = -\left[\frac{dX_{CS,READILY}}{dt} + \frac{dX_{CS,SLOWLY}}{dt}\right] = kdis_{XcsR} \cdot X_{CS,\ READILY} + kdis_{XcsS} \cdot X_{CS,\ SLOWLY}\ .$$

ere $kdis_{XcsR}$ is the disintegration kinetic of the slowly biodegradable fraction
$kdis_{XcsS}$ is the disintegration kinetic of the readily biodegradable fraction
X_{CS}, $X_{CS,READILY}$, $X_{CS,SLOWLY}$ are the total, readily and slowly particulate substrate

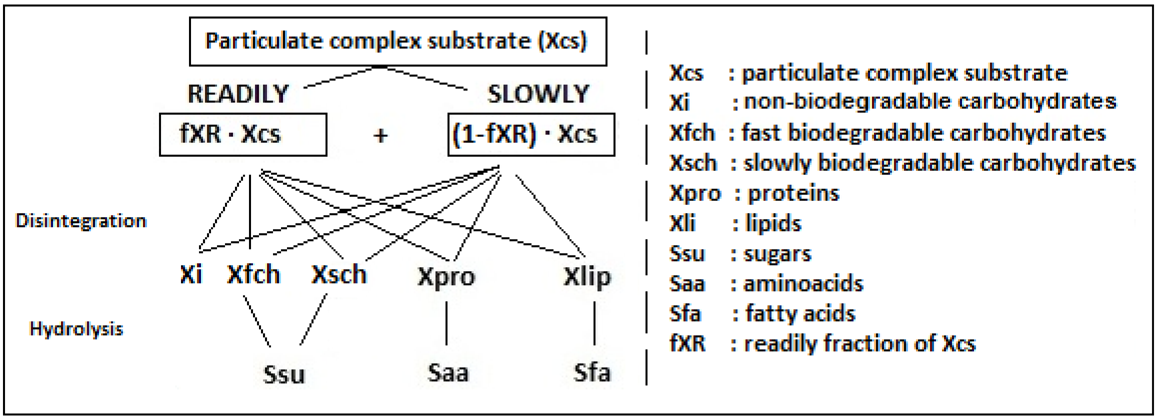

Figure 1. Proposed mechanism for particulate disintegration in the ADM1-based AcoD model.

Fractionation. Readily and slowly biodegradable fractions

Readily fractions f_{XR} can be estimated from batch assays. By applying derivatives to batch curves, the area below the curve is proportional to the total organic matter added to the system. Then, it is easy to determine what area belongs to readily fraction and what to slowly fraction, assuming disintegration as the rate-limiting stage of the AD. Even though there is not a rule to split the area into the two fractions, it will be assumed that readily fraction ends when the biogas production rate changes sharply (Figure 2).

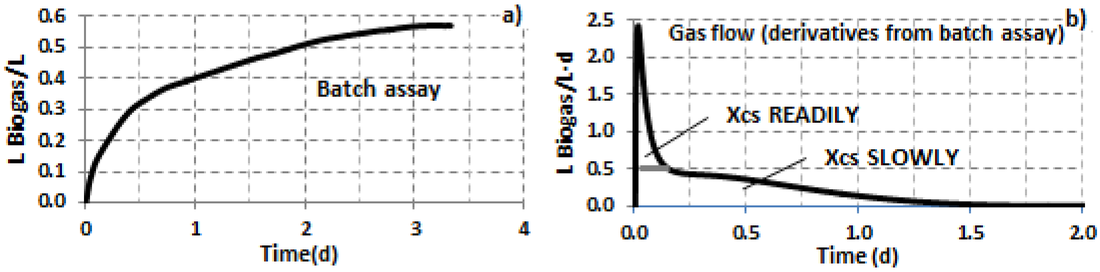

Figure 2. Biogas production curves, example for an assay curve of cauliflower a) Cumulative biogas production. b) Gas production rate (computed from cumulative derivative).

Characterisation and non-biodegradable fraction

The characterisation of each FVW was obtained from *APRIFEL* (http://www.aprifel.com). FVW are mainly made of carbohydrates, protein, lipids and fibres. Fibres include hemicellulose and other non-biodegradable polymers of carbohydrates. Parts of the fibres were considered in the model as slowly biodegradable carbohydrates (X_{sch}), and the rest as non-biodegradable (X_i) to ensure the final BMP value of the batch assay. Once the non-biodegradable fraction is adjusted, the kinetic parameters for disintegration-hydrolysis are manually tuned to fit experimental batch (Figure 3.a/b).

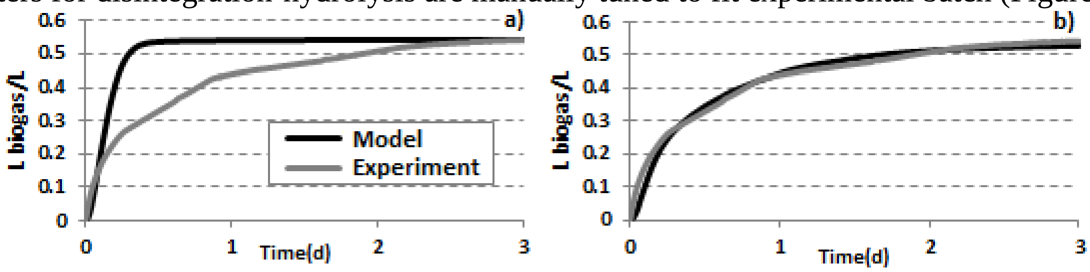

Figure 3. a) Experimental and simulated batch experiment of mango (using overestimated disintegration and hydrolysis parameters to adjust the slowly and non-biodegradable content of fibres and ensure the final BMP value is achieved. b) Experimental and simulated batch of mango after kinetic parameter calibration.

Model calibration for continuous AcoD process

The readily fractions f_{XR} obtained graphically from derivatives of batches (as in Figure 2.b) had to be calibrated for the model to fit the experiments. The calibrated values after model calibration differed from those initially obtained from the graph. The new proposed graphical approach to estimate the readily fractions was tested: considered for all FVW the same threshold of 250 mL biogas/L·d to split the readily and slowly fraction areas (or around 20 mL biogas/L·d·gVSS, since batch assays were carried out at 13 g VSS/L). See Table 1. In the case of potato, f_{XR} values differed largely. The hypothesis that disintegration controls the overall reaction might be not true for potato.

Table 1. Readily fraction values obtained with the model and graphically and % non-biodegradable fibres.

Substrate	f_{XR} (model)	f_{XR} (BMP derivatives)	% non-biodegradable fraction of fibres
Lettuce	0.35	0.22	100
Potato	0.00	0.19	100
Apple	0.40	0.41	70
Carrot	0.50	0.41	10
Banana	0.39	0.39	0

The same set of kinetic parameters for disintegration of particulate substrates ($kdisX_{csR}$, $kdisX_{csS}$) and hydrolysis of slowly and fast biodegradable carbohydrates, X_{sch} and X_{fch},, proteins, X_{pro}, and lipids, X_{li}, (k_{hyd_Xsch}, k_{hyd_Xfch}, k_{hyd_Xpro}, k_{hyd_Xli}) were used to calibrate the model and fit batch assays.

Table 2. Disintegration and hydrolysis kinetic parameters applied in the model

$k_{disXcsS}$ (h^{-1})	$k_{disXcsR}$ (h^{-1})	k_{hyd_Xsch} (h^{-1})	k_{hyd_Xfch} (h^{-1})	k_{hyd_Xpro} (h^{-1})	k_{hyd_Xli} (h^{-1})
0.07	2.50	0.04	0.417	0.417	0.05

Batch assays of lettuce, potato, apple, carrot and banana among other FVW were simulated with the kinetic parameters and readily and non-biodegradable fibre fractions values from Tables 1, 2. These simulated batches (not shown) fitted satisfactorily the experimental assays with results similar to those in Figure 3.b.

A continuously operated digester treated the five substrates simultaneously during 15 weeks. The process was simulated with the AcoD model, including the kinetic modifications above, for its validation for solid wastes. The disintegration and hydrolysis kinetic parameters obtained from the batch assays were used leaving the rest of parameters constant in its standard ADM1 values.

Figure 4 shows a satisfactory model simulation of the experimental results in terms of methane production, volatile solids, pH and alkalinity. In both experiment and simulation, VFA were negligible and biogas composition around 55% of CH_4.

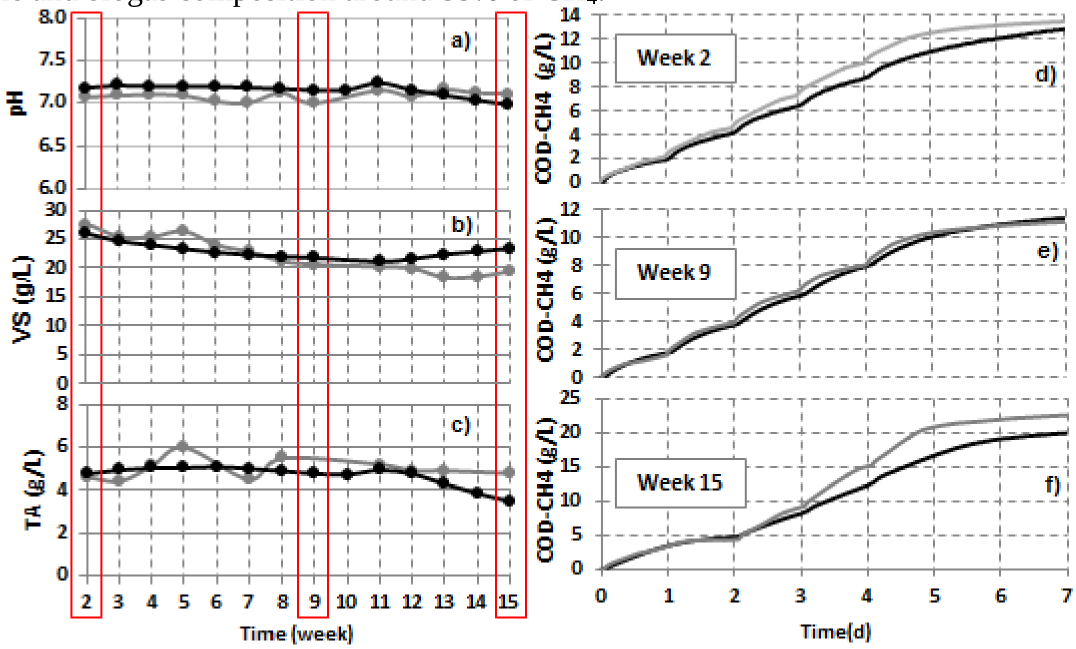

Figure 4. a) pH, b) volatile solids (VS), c) total alkalinity (TA) and d) e) and f) cumulative methane production (COD equivalents) in week 2, 9 and 15, at OLR of 2.0, 2.0 and 4.7 g VS/kg·d, respectively.

CONCLUSIONS

The fractionated disintegration kinetics proposed for solid substrates proved adequate to describe batch experiments. The parameters obtained from single substrate batch studies provided good simulation results in continuous codigestion of multiple substrates. This provides an avenue to incorporate kinetic information from batch tests of individual substrates into an AcoD model.

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