



Regular article

Variable kinetic approach to modelling an industrial waste anaerobic digester



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ARTICLE INFO

Article history:

Received 4 August 2014

Received in revised form 23 October 2014

Accepted 24 December 2014

Available online 27 December 2014

Keywords:

Anaerobic processes

Biodegradation

Biogas

Modelling

Monte carlo

Kinetic parameters

ABSTRACT

Anaerobic co-digestion of agro-industrial wastes is a promising option for the stabilisation of residues with biogas production. A mixture of bovine ruminal content, tannery carving fat and activated sludge purge was considered for this study. Biodegradability tests for individual wastes and a mixture of wastes were performed in batch conditions. Additionally, a completely mixed reactor with an average residence time of 30 days and a loading rate of 3.0 gVS/L.d. was employed for the mixture of wastes. A Volatile Solids (VS) removal efficiency of 66% with a methane production of 0.38 L_{CH₄}/kgVS_{added} or 0.58 L_{CH₄}/kgVS_{removed} was attained. A first-order kinetic model with lag time was employed to describe the behaviour of the batch tests. Parameter determination was performed using direct search methods. Monte Carlo methods were utilised to determine the range of parameters. An ultimate methanation of 90 ± 6% was obtained from the batch tests. For the continuous system, a simple model with a variable kinetic constant that reflects the microbiological activity was proposed. The model was calibrated by adjusting the stoichiometric coefficients using solids outlet data, and the kinetic constant was deduced using experimental methane flow data. The kinetic constant doubles for approximately four residence times, which demonstrates the acclimation of biomass.

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1. Introduction

At present, global changes in the world like minimization of greenhouse gases emissions, and the need of use renewable energy sources require a more efficient use of biotechnologies [1,2]. The sustainability principles must be present in our technological decisions without detriment of other technical and economic considerations. In this sense, the anaerobic digestion of agro-industrial organic waste is an alternative treatment with significant advantages, such as low operating costs and power generation from biogas [3,4]. Additionally, anaerobic technology has proven to be more favourable than the aerobic treatment of wastes from the point of view of greenhouse gas generation [5] and can even compete with other biofuels [6]. In this scenario, anaerobic digestion plays a key role because the products generated (e.g., hydrogen, methane) from the different metabolic steps can be used as energy sources in boilers, internal combustion engines or fuel cells [7] or as raw material for other processing options (e.g., the production of biopolymers or other organic substances). For these reasons, anaerobic

technology constitutes the core of organic waste treatment systems [8].

A constraint of the high-load operation is the presence of inhibitors, which are produced by the waste [9–11]. For instance, this constraint is found in the fat carving generated by tanneries, which contains a high concentration of fat that is abundant in triglycerides; the triglycerides degrade during digestion to glycerol and long-chain fatty acids. Additionally, long-chain fatty acids are potential inhibitors of methanogenesis [12,13].

Other wastes, such as ruminal content and secondary sludge from aerobic wastewater treatment plants, exhibit low methane generation potential due to their low biodegradability. With respect to the ruminal concentration, a high-fibre content hinders mixing if its size is not reduced by pretreatment [14]. This situation compels the digesters to operate with low-solid concentrations to limit the potential for high loads.

Co-digestion is a widely used way in order to enhance the anaerobic degradations of solid substrates. The most reported experiences are related to agroindustrial or agricultural wastes and the organic fraction of municipal solid wastes, but also the sludge from aerobic facilities is considered [15]. The mixture of wastes with different characteristics, enrich the substrate composition, dilutes the inhibitory components, prevents mixing problems and enhances methane generation [15–17].

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Nomenclature

List of symbols

k	first order kinetic constant [d ⁻¹]
k_m	first order kinetic constant in continuous model [L/gVS.d]
k_1	stoichiometric coefficient from solids to methane conversion [LCH ₄ /gVS]
k_3	stoichiometric coefficient from solids to microorganisms conversion [-]
L	Laplace transform
M	accumulated methane production [mL]
M_0	ultimate methane production [mL]
q_{CH_4}	methane flow [L/L _{reactor} .d]
r_M	methane production rate [gCOD/L.d]
r_X	solid substrate degradation rate [gVS/L.d]
t	time [d]
X	solid substrate concentration [gVS/L]
X_b	biodegradable solid substrate concentration [gVS/L]
X_m	microorganisms concentration [gVS/L]
X_{nb}	non biodegradable volatile solid concentration [gVS/L]
X_t	total volatile suspended solids [gVS/L]
$Y_{X/M}$	yield coefficient, conversion of substrate into methane [gCOD methane/gVS]
θ	lag time for microbial activation[d]

Despite increasing anaerobic applications, the comprehensive and practical modelling of these systems is still developing. An important milestone in this field was the development of the IWA (International Water Association) ADM1 model (Anaerobic Digestion Model 1) [18]. This structured model included multiple steps describing the biochemical and physicochemical processes, which involved at least 26 dynamic state variables and many parameters. Although the complexity of anaerobic processes was reflected in the ADM1 model, direct applications for modelling and control purposes are difficult to use. Additionally, the identification of model parameters under actual operational conditions is difficult. The ADM1 model also fails to depict all complex phenomena that occurs in an anaerobic system and must be expanded to include other phenomena [19]. Simpler models with reduced sets of state variables and parameters have been proposed [20–23]. Although simple models do not represent the complexity of real processes, the identification of parameters and model validations are more straightforward [24–26].

As a rule, hydrolysis is the rate limiting step in the degradation of solid wastes. A first order kinetic rate with respect to the substrate is widely accepted for this step [27]. The simplest kinetic model for the overall process is a first order kinetic expression. Several experimental procedures could be planned in order to obtain the model parameters, both in batch mode [28] or in continuous mode [29]. Specially, Biochemical Methane Potential (BMP) tests [28] are standard tests that could be easily extended in order to obtain kinetics parameters.

Even though simple optimisation techniques, such as least squares methods, are widely used in order to obtain the model parameters, these methods do not provide information about the confidence interval of results. Standard deviations are obtained by repeated measures. This option increases the experimental work and consumes resources. Alternatively, simulation methods that only consume computational time, such as Monte Carlo, can be applied [30,31]. The performance of the Monte Carlo confidence interval method is comparable to other widely accepted methods

of interval construction, and it can be used when only summary data are available [32].

In chemical systems, kinetics parameters obtained from batch experiences are used without restrictions to design continuous systems. However systems that involves microorganisms must take into account the acclimation phenomena. Then, kinetics parameters could change through time in order to reflect the acclimation or to reflect adverse microbiological conditions. In very simple models, lumping a complex behaviour in one single parameter, variation of this parameter could reflect the environmental conditions.

The objective of this study is to evaluate the application of a simple kinetic model to describe the co-digestion of three agro-industrial wastes (ruminal content, tannery carving fat and biological sludge). The first order kinetic model is validated in batch using standard experiences and the confidence range of parameters was determined using Monte Carlo techniques. The model is validated also in continuous conditions, but in this case a variable kinetic parameter is postulated describing the acclimation capacity of microorganisms.

2. Model

Biodegradability tests are typically performed in batch conditions [28]. The solid substrate and anaerobic sludge (inoculum) are placed in batch reactors in anaerobic conditions. Cumulative methane production is monitored over time and the ultimate value is used to calculate the methane potential. The transformation of solid substrate into methane involves a complex series of sub-transformations, whereas hydrolysis determines the total kinetics. Typically, a single first-order kinetic model is used to represent the hydrolysis of particulate matter [27]. Despite the complex phenomena involved, biodegradability curves can be fit to a simple first-order kinetic model.



where

$$r_x = kX \quad (2)$$

where k is the first-order kinetic constant, and X is the solid substrate concentration. The methane accumulative curve asymptotically approaches a value, which indicates the maximum fraction of substrate that can be transformed into methane. The stoichiometric coefficient $Y_{X/M}$ relates the rate of substrate degradation to the rate of methane production. If both substances are expressed by the same units (e.g., grams of COD), this stoichiometric coefficient is the methanation yield of the solid substrate.

$$r_M = Y_{X/M} r_X \quad (3)$$

The accumulated methane curve is

$$M = M_0(1 - e^{-kt}) \quad (4)$$

where M is the accumulated methane, M_0 is the maximum quantity of methane that can be obtained, and t is the time elapsed after the lag time θ . The lag phase that occurs at the beginning of the curves in batch tests is attributed to the microorganism requirements for acclimation or the need for activation of the biological activity. Thus, by fitting this model to the experimental data, the kinetic constant k and the asymptotic value M_0 can be obtained ($Y_{X/M}$ can be obtained if the initial amount of substrate is known).

Continuous systems require another approach. First, a virtually complete mix can be assumed due to the mechanical stirring device. The system can be considered to be a lumped parameter system, and the mass balance equations can be performed considering the entire reactor as a control volume. Second, the system is not truly a continuous reactor: the feed and the discharge are performed once

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