

# Modelling of a batch anaerobic digestion

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The Anaerobic Digestion Model no 1 (ADM1) has been implemented to simulate batch fermentation. The pH changes and inhibition of the fermentation have been studied. The model has been used to investigate the effects of substrate composition and concentration as well as the composition of the microorganism population on the course of fermentation. The overload of a reactor has been discussed.

**Keywords:** anaerobic digestion, ADM1 model, batch fermentation.

## INTRODUCTION

Anaerobic digestion of organic wastes and by-products from the agricultural and food industry is a process known for many years and widely used for waste stabilization. Anaerobic digestion has become a key method for both waste treatment and the production of renewable fuels. Biogas is produced mainly from manure, organic waste from household, food and agro industry and energy crops<sup>1</sup>.

With the increasing complexity of the digestion processes, increased effort is needed to evaluate the impact of the process variable changes on the digesters' performance. Recently, the International Water Association's (IWA) Task Group has developed a generic anaerobic digestion model, Anaerobic Digestion Model No. 1 (ADM1) to address these issues<sup>2</sup>. The model consists of a number of processes to simulate all possible reactions occurring in anaerobic sludge including not only biological reactions, such as disintegration, hydrolysis of suspended solid, uptake (growth) and decay of microorganisms, but also physico-chemical reactions, including ion association/dissociation and liquid-gas transfer. In total, 19 processes, 24 components, and 56 relative stoichiometric and kinetic parameters were assumed for biological processes, while additional processes and parameters were determined for physico-chemical processes. The ADM1 has been implemented for the modelling of anaerobic treatment of a wide range of waste streams in continuous reactors<sup>3</sup>.

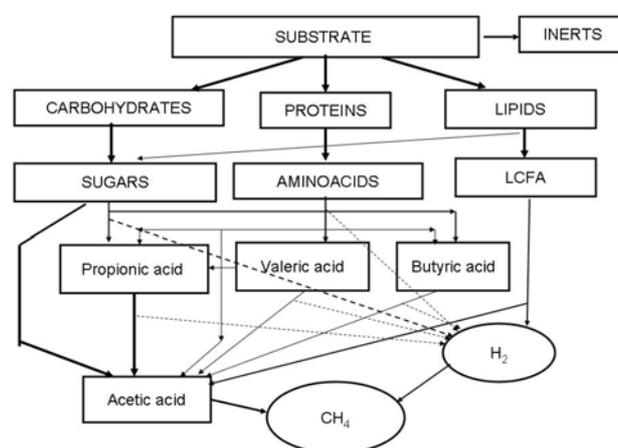
In the present study the ADM1 was used to investigate a batch process. The high organic load in batch fermentation may inhibit methane production due to high accumulation of organic acids. The ADM1 has been used to simulate pH changes in batch operation and investigate the influence of pH on the process stability.

## THE ADM1 MODEL

The ADM1 model is described in considerable detail in the report prepared by the IWA Task Group for Mathematical Modeling of Anaerobic Digestion Processes<sup>4</sup>. The following provides a brief overview of the model for the purposes of this implementation.

The ADM1 model is a structured model that reflects the major processes that are involved in the conversion of complex organic substrates into methane and carbon dioxide and inert byproducts. In Fig. 1 an overview of the substrates and conversion processes that are addressed by the model is presented. The disintegration of complex solids into inert substances, carbohydrates, proteins and fats is the first step of the process. The products of disintegration are hydrolyzed to sugars,

amino acids and long chain fatty acids (LCFA), respectively. Carbohydrates and proteins are fermented to produce volatile organic acids (acidogenesis) and molecular hydrogen. LCFA are oxidized anaerobically to produce acetate and molecular hydrogen.



**Figure 1.** A schematic diagram of biochemical processes in ADM1

Propionate, butyrate and valerate are converted to acetate (acetogenesis) and molecular hydrogen. Methane is produced by both cleavage of acetate to methane (acetoclastic methanogenesis) and reduction of carbon dioxide by molecular hydrogen to produce methane (hydrogenotrophic methanogenesis). To address these mechanisms, the model employs state variables to describe the behaviour of soluble and particulate components. All organic species and molecular hydrogen are described in terms of chemical oxygen demand (COD). Nitrogenous species and inorganic carbon species are described in terms of their molar concentrations. Soluble components are those that can pass through microbial cellular walls and include the monomers of complex polymers (sugars, amino acids, long chain fatty acids), volatile organic acids (propionate, butyrate, valerate, acetate), hydrogen, and methane. In addition to the organic species, the model addresses inorganic carbon (carbon dioxide and bicarbonate) and nitrogenous species (ammonia and ammonium). All of the species that dissociate as a function of pH (VFAs and ammonia) have variables defined for both the protonated and non-protonated species. A dissociation equilibrium for all these compounds has been assumed.

The microbial species that are considered in the model include sugar fermenters, amino acid fermenters, LCFA oxidizers, butyrate and valerate oxidizers, propionate oxidizers, acetoclastic methanogens and hydrogenotrophic methanogens.

Substrate conversion processes are described by a number of kinetic expressions that describe the conversion rates in terms of substrate concentrations and rate constants. All biochemical extracellular steps were assumed to be first order. Substrate uptake Monod-type kinetics is used as the basis for all intracellular biochemical reactions. Biomass growth is implicit in substrate uptake. The other uptake-regulating functions are secondary Monod kinetics for inorganic nitrogen (ammonia and ammonium), to prevent growth when nitrogen is limited, and competitive uptake of butyrate and valerate by the single group that utilises these two organic acids.

It is recognized that a number of the conversion processes that are active in anaerobic digestion can be inhibited by the accumulation of intermediate products such as molecular hydrogen, ammonia or extreme pH levels. In the model, all microbially mediated substrate conversion processes are subject to inhibition by extremes in pH. All anaerobic oxidation processes are subject to inhibition by the accumulation of molecular hydrogen and acetoclastic methanogenesis is inhibited at elevated free ammonia concentrations. Hydrogen and free ammonia inhibition are represented by non-competitive functions.

## THE MODEL IMPLEMENTATION

This study has been based on the differential equation (DE) implementation of the ADM1 model, including 24 components, 12 biological processes and 5 acid-base processes. The effect of substrate overload has been the main goal of simulation. Therefore the decay of microbial biomass has been omitted.

The most important acid-base pairs in anaerobic systems are:  $\text{NH}_4/\text{NH}_3$  ( $\text{pK}_a = 9.25$ ),  $\text{CO}_2/\text{HCO}_3^-$  ( $\text{pK}_a = 6.35$ ), and  $\text{VFA}/\text{VFA}^-$  ( $\text{pK}_a \sim 4.8$ ), as well as the  $\text{H}_2\text{O}/\text{OH}^-/\text{H}^+$  system ( $\text{pK}_w = 14.00$ ) [4]. Inorganic phosphorous has been included to the charge balance ( $\text{H}_3\text{PO}_4/\text{PO}_4^{2-}$ ). The pH calculation was incorporated by means of cations, hydroxyls and water. Because dissociation/association processes are very rapid compared with other reactions (especially biochemical), they

were referred to as equilibrium processes and described by algebraic equations.

An empirical correlation was employed as a process rate multiplier to reflect the effects of extreme pH.

$$I(\text{pH}) = \frac{1 + 2 \cdot 10^{0.5(\text{pH}_{\text{LL}} - \text{pH}_{\text{UL}})}}{1 + 10^{(\text{pH} - \text{pH}_{\text{UL}})} + 10^{(\text{pH}_{\text{LL}} - \text{pH})}} \quad (1)$$

where  $\text{pH}_{\text{LL}}$  and  $\text{pH}_{\text{UL}}$  are lower and upper limits of pH, respectively.

The values of the model parameters were set as suggested in the Scientific and Technical Report of AD<sup>4</sup>.

The mass balances for the model components in a batch operation are given by

$$\frac{d\mathbf{X}}{dt} = \mathbf{N} \cdot \mathbf{R}(\mathbf{X}) \quad (2)$$

where  $\mathbf{X}$  is a vector of state variables,  $\mathbf{N}$  – coefficients matrix and  $\mathbf{R}(\mathbf{X})$  vector of microbial transformations rates.

The boundary conditions for the set of differential equations (2) consist of initial concentration of a substrate and initial concentration of biomass. In simulations the equal distribution of initial biomass among all groups of microorganisms has been assumed.

The set of differential equations (2) was solved numerically by the fourth order Runge-Kutta-Gill methods implemented in the MathLab package. The nonlinear equation for pH calculation was solved by the Newton method at each step of integration.

## THE RESULTS OF SIMULATION

Figure 2 presents the results of simulations of batch fermentation for various initial concentrations of carbohydrate substrate. The initial concentration of microorganisms was equal to the organic load ( $F/M = 1$ ). The increase of organic load disturbs the fermentation due to a drop in pH. The low pH mainly inhibits the activity of methanotrops.

For low organic load the biogas production follows typical saturation curves described by the first order kinetics<sup>5</sup>:

$$V = V_{\text{max}} (1 - e^{-kt}) \quad (3)$$

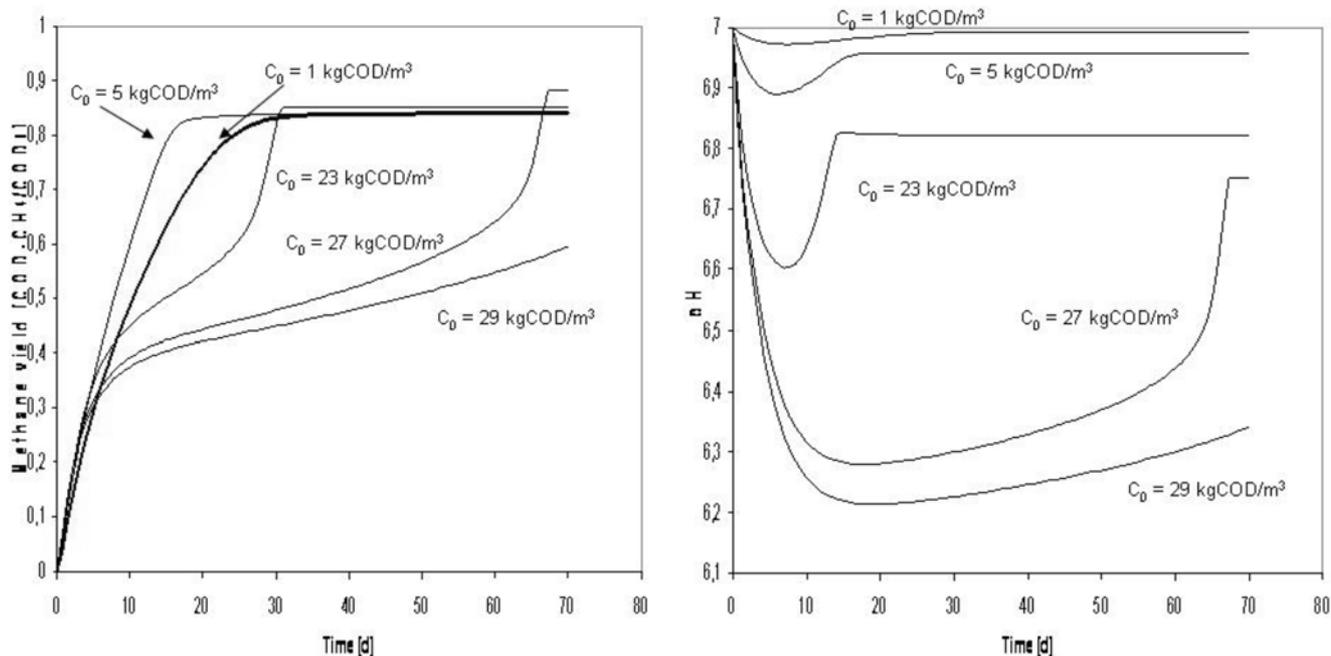


Figure 2. The effect of initial organic load on methane yield and pH

Figure 3 presents an approximation of simulated methane production (dotted line) by linearization of eq. (3) (solid line). The figure indicates that for non-disturbed fermentation simple first order kinetics may be a good approximation of methane production. It is noteworthy that the first order kinetic constant calculated from simulation data is equal  $k = 0,102 \text{ d}^{-1}$ , whereas the value of hydrolysis constant of carbohydrate taken into simulation is equal  $0.25 \text{ d}^{-1}$ . The result shows that an estimation of the hydrolysis rate provided by a measurement of biogas production would lead to inaccurate values for the hydrolysis constant.

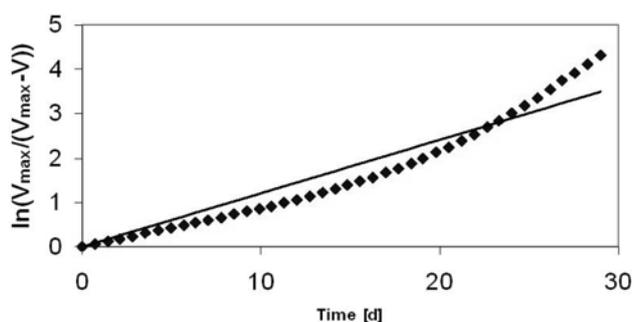
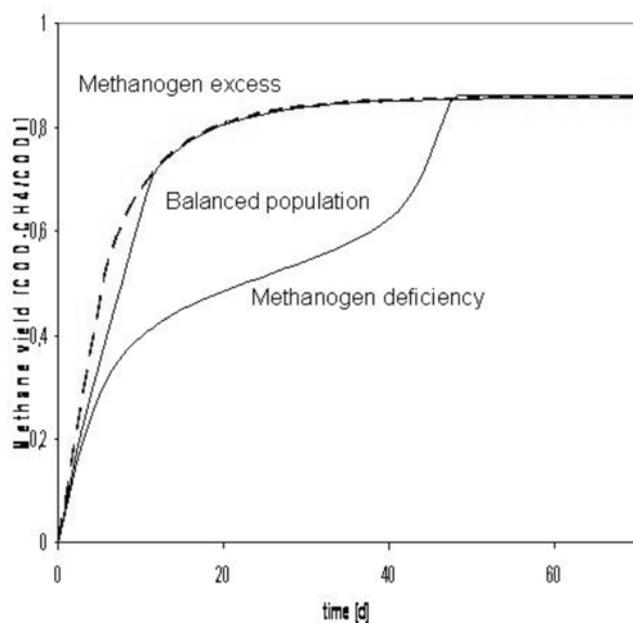


Figure 3. Comparison of simulation and linearized eq. (3)

Figure 4 presents the results of simulated batch fermentation with constant initial load of carbohydrates  $27 \text{ kg COD/m}^3$  and a different microbial population composition. The microbial population was divided into three groups: hydrolysing and acidogenic bacteria (group 1: sugar fermenters, amino acid fermenters, LCFA oxidizers), acetogenic bacteria (group 2: butyrate and valerate oxidizers, propionate oxidizers), and methanogens (group 3: acetoclastic methanogens and hydrogenotrophic methanogens). The total initial concentration of microorganisms was equal to the organic load ( $F/M = 1$ ). Three cases were considered: balanced population (equal mass of all three groups of microorganisms), methanogen deficiency (the ratio of group 1: group2: group3 was equal 1:2:1 or 2:1:1) and methanogen excess (group1:group2: group3 equal 1:1:2). The fermentation is disturbed in the case of low fraction on methanogens in microbial population. The calculations show that the fraction of methanogens in overall mi-



crobial population is important. The same simulation results were obtained for methanogen deficiency both in the case of an excess of group 1 (group rate equal 2:1:1) and with an excess of group 2 (group rate 1:2:1). Similar results have been reported in experiments involving transient loading of a continuously stirred tank reactor<sup>6</sup>.

Figure 5 presents the results of batch fermentation simulations for selected compositions of the substrate. It has been assumed that the substrate consisted of hydrocarbons and fats. The total organic load was constant and equal to  $27 \text{ kgCOD/m}^3$ .

A carbohydrate high COD load leads to the inhibition of fermentation. The addition of 10% of lipids to the substrate does not change the situation – the reactor is overloaded. Fermentation is improved in a substrate consisting of 40% of lipids, the result of slower hydrolysis of lipids than carbohydrates. Acids concentration grows slower in a substrate with lipid growth and reaches lower values than for pure carbohydrates (fig. 6). The simulation results support the experimental observations that co-fermentation of carbohydrates with fatty substrates leads to better and stable biogas production<sup>7</sup>.

## SUMMARY

- The Anaerobic Digestion Model 1 is a powerful tool for modelling biogas production and to study the effects of the process parameters on the process performance.
- Reactor overload causing a pH drop below 6.7 inhibits methanogen activity and disturbs the fermentation process.
- Methanogen deficiency may lead to fermentation disturbance or inhibition.
- The addition of fats to the carbohydrate substrate increases the stability of the fermentation process.

## ACKNOWLEDGEMENT

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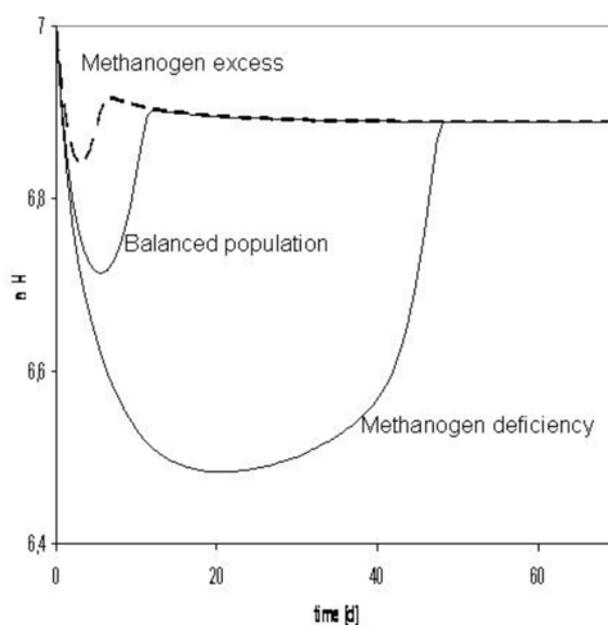


Figure 4. The effect of microbial population composition on methane production

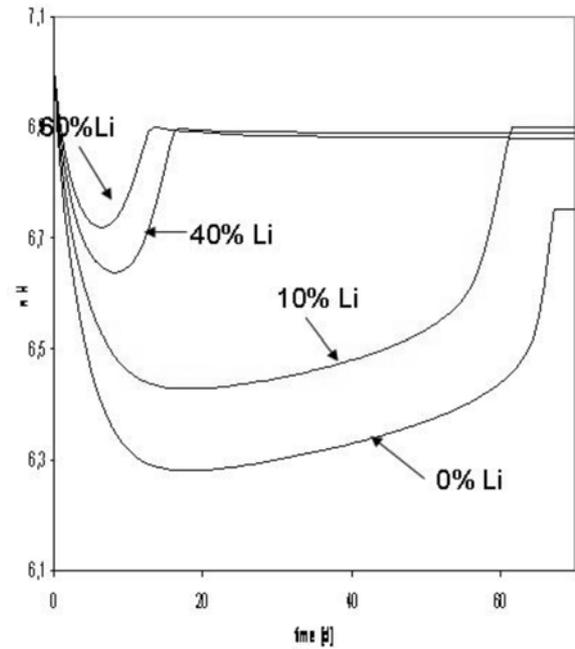
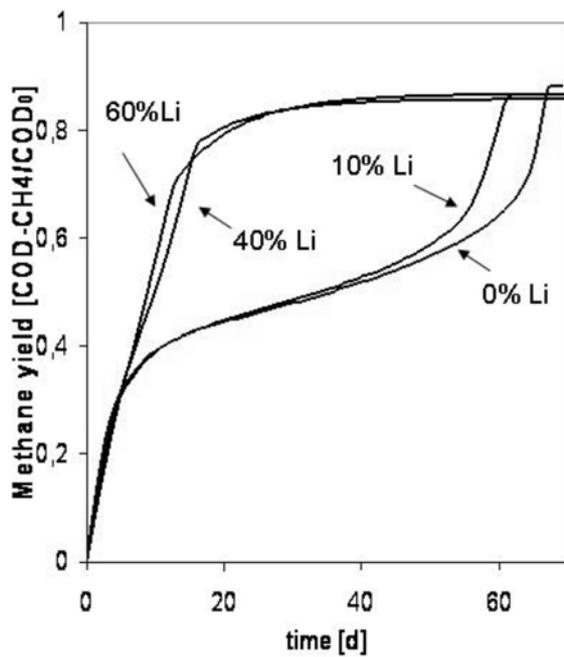


Figure 5. The effect of substrate composition on methane production

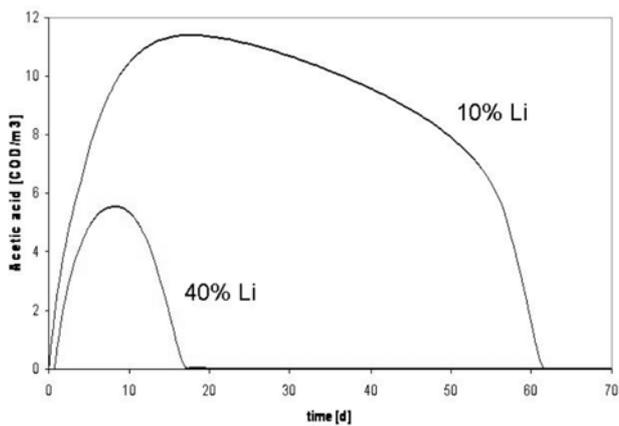


Figure 6. The acetic acid concentration for different fraction of lipids in carbohydrate – lipid fermentation

**SYMBOLS**

- $k$  – first order kinetic constant,  $d^{-1}$
- $N$  – stoichiometric coefficient matrix
- $R(X)$  – vector of microbial transformation rates
- $t$  – time, d
- $V$  – methane volume,  $m^3$
- $V_{max}$  – maximum methane production,  $m^3$
- $X$  – state variables vector

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