Modeling Anaerobic Codigestion of Cheese Whey with Poultry Manure

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Abstract: - A mathematical model describing the combined anaerobic digestion of cheese whey with poultry manure is presented. The model distinguishes three enzymatic processes (hydrolysis of proteins, lipids and cellulose, respectively) and six bacterial groups: sugars and amino-acids fermentors, fatty acids oxidisers, acetogens, aceticlastic methanogens and hydrogentrophic methanogens. For the solution of the model (set of non-linear differential equations) a fully implicit finite difference scheme is applied, with the exemption of bacteria increasing rates that are explicitly introduced. The model is proved to be under condition stable (limited time increment required) while the initial conditions that are assumed are critical for its stability, too. The model is validated according to data from an existing pilot unit. Based on this model, co-digestion of whey with poultry manure is further examined.

Key-Words: - Anaerobic digestion; Codigestion; Modeling; Stability; Cheese whey; Poultry manure;

1 Introduction

Buswell made a series of co-digestion experiments back in early '30s, treating manure in combination with most possible types of organic waste (Buswell and Hatfield, 1936). In anaerobic co-digestion, a co-substrate is used that may improve the biogas yield due to possible synergism between the bacterial group and the supply of missing nutrients. Some other advantages are also attributed to the process as economic benefits from the fact of sharing equipment, easier handling of mixed waste, the use of common facilities and economy of scale (Mata-Alvarez et al., 2000). For these reasons, co-digestion has been applied at commercial scale. As example, anaerobic digestion of manure with industrial organic waste has been widespread in Denmark where around 20 big centralized plants have been erected since the late 1980s with very positive results (Danish Energy Agency, 2000).

In general, various substrates can be co-treated. However, systematic experiments should always be preceded to confirm that no competitive or other inhibiting factors arise. An interesting waste combination for co-treatment, for areas with cheese making activities and poultry raising units (like several places for instance in Greece) is cheese whey with poultry manure. Indeed, manure alone has high ammonia content that causes inhibition to methanogenesis. On the other hand, if whey is treated alone it leads to the production of volatile acids that may decrease pH and cause instability to the process. Their combination instead dilutes ammonia, improves C:N ratio in both substrates and offers the necessary buffer capacity to cope with the volatile acids produced from the whey. Due to these advantages, various relevant experiments were performed in the past by, for instance, Desai et al. (1994) and Ghaly (1996), without however any attempt to model the processes.

Indeed, although anaerobic codigestion has been modeled for various combinations, like the organic fraction of municipal sewage waste with primary sewage sludge (Kyeli et al., 1997), manure with olive oil mill effluent (Angelidaki et al., 1997) etc., this is not the case for the combination under consideration. To this aim, a detailed model is developed here, distinguishing the specific composition for each waste and the various bio-chemical processes that take place in the digester. The model is firstly validated according to a pilot plant production data, and is afterwards applied for the further examination of whey/manure co-digestion.

2. Problem Formulation

2.1 Model Description

The suggested model for anaerobic co-digestion of whey with manure involves:

- three enzymatic processes, namely hydrolysis of proteins to amino acids, hydrolysis of lipids to long chain fatty acids (LCFA) and hydrolysis of cellulose to sugars
- five bacterial groups namely fermenting acidogens, oxidizing (LCFA degrading

acidogens), acetogens, aceticlastic, and hydrogentrophic methanogens.

The following equations (1) to (9) present conversions that take place, together with the relevant stoichiometry, expressed in COD units:

proteins → amino acids (1)

lipids → LCFA (2)

cellulose → sugars (3)

amino acids → 0.6 propionate + 0.4 acetate (4)

sugars → 0.667 acetate + 0.333 hydrogen (5)

LCFA → 0.538 propionate + 0.308 acetate + + 0.154 hydrogen (6)

propionate → 0.571 acetate + 0.429 hydrogen (7)

acetate → methane (8)

hydrogen → methane (9)

The proteins, lipids and cellulose in the feed are enzymatically hydrolyzed to amino acids, LCFA and sugars, respectively (as indicated in eq. (1) to (3)). The amino acids and sugars are fermented to propionate, acetate and hydrogen, according to eq. (4) and (5), while the LCFA are oxidized to propionate, acetate and hydrogen, as per eq. (6). The propionate is further degraded to acetate and hydrogen, by acetogen bacteria, eq. (7). Last, the acetate and hydrogen are converted to methane by acetoclastic and hydrogentrophic methanogen bacteria, respectively, as shown in eq. (8) & (9)

Eq. (4) to (9) are below written in the form of chemical reactions as eq. (4.a) to (9.a), allowing additionally to express mole stoichiometry for CO_2 and hydrogen gas, that are also produced and participate in biogas.

$$C_5H_7O_2N+2.571H_2O \rightarrow 0.857\ C_2H_5COOH + +CH_3COOH + 0.429CO_2 + NH_3 \quad (4.a)$$

$$C_{12}H_{22}O_{11}+5H_2O \rightarrow 4CH_3COOH+4CO_2+8H_2 \quad (5.a)$$

$$C_4H_9COOH+2H_2O \rightarrow C_2H_5COOH + 2H_2 + +CH_3COOH \quad (6.a)$$

$$C_2H_5COOH+2H_2O \rightarrow CH_3COOH+CO_2+2H_2 \quad (7.a)$$

$$CH_3COOH \rightarrow CH_4+CO_2 \quad (8.a)$$

$$CO_2+4H_2 \rightarrow CH_4+2H_2O \quad (9.a)$$

All hydrolysis reactions are assumed to follow first order kinetics. So, for instance, hydrolysis of proteins takes the form:

$$\frac{d[Protein]}{dt} = - K_{H,Protein} \cdot Protein \quad (10)$$

where the left term is the rate of hydrolysis (time derivative), $K_{H,Protein}$ is hydrolysis constant (d^{-1}) and *Protein* is the protein concentration ($g \cdot m^{-3}$).

Monod kinetics is applied to all other reactions, including substrate inhibition. For instance, rate of anaerobic oxidation of LCFA is expressed as:

$$\frac{d[LCFA]}{dt} = \frac{\mu_{O,MAX} \cdot C_O / Y_O}{1 + K_{SO} / LCFA} \quad (11)$$

where $\mu_{O,MAX}$ is maximum specific growth rate of anaerobic oxidizing bacteria (d^{-1}), C_O is bacteria concentration (g-VSS/m^3), Y_O is biomass yield (g-VSS/g-COD) and K_{SO} is saturation constant (g-COD/m^3). A non competitive acetic acid inhibition term is included for the fermentation reaction, while a competitive acetic acid inhibition term is introduced for the acetogenic reaction.

Values for the parameters of the model were taken from Ristow and Hansford, 2001 (who however had not included CO_2 production in their model, neither differentiated between sugars and amino-acids fermentations), and Kalyuzhnyi and Fedorovich (1998). The values for typical mesophilic conditions (35°C) are presented in table 1, while for other temperatures the kinetic constants may be adapted according to Arrhenius type temperature dependence (e.g. almost doubling for every 10°C increase and vice versa).

2.2 Solution of the model

The simulator consists of a mathematical non-linear system of differential equations with fourteen state variables, namely nine for the substrates and other constituents and five for the biomasses. To solve it, a finite difference scheme is applied as follows:

- fully implicit for all concentrations (including constituents and microbial populations)
- explicit for the bacteria growth rates (in order to get a linear system of algebraic equations for each time step).

The solver proved to be under condition stable, and so a very small time step was needed to be applied, e.g. in the order of 1 sec. However, as no complicated calculations are needed, simulation

proceeds very quickly, despite the small time increment.

It was also realized that the simulator was very sensitive to the assumed initial conditions. To cope with this problem, we firstly calculated the equilibrium (steady state) values of the variables for the initial conditions and introduce these values as initial conditions. Starting with initial equilibrium values, simulation proceeded without any instability trends.

Table 1. Main reactions and parameter values of the model (for 35°C reactor temperature)

hydrolysis of proteins	K_H=0.104d^{-1}
hydrolysis of lipids	K_H=0.118d^{-1}
hydrolysis of cellulose	K_H=0.146d^{-1}
fermentation of sugars and amino-acids *(with acetate inhibition)*	μ_{MAX}=5.559d^{-1} K_S=28gCOD/m^3 K_I=604gCOD/m^3 Y=0.043gVSS/gCOD
anaerobic oxidation	μ_{MAX}=0.382d^{-1} K_S=1.816gCOD/m^3 Y=0.11gVSS/gCOD
acetogenesis *(with acetate inhibition)*	μ_{MAX}=0.111d^{-1} K_S=247gCOD/m^3 K_I=181gCOD/m^3 Y=0.018gVSS/gCOD
aceticlastic methanogenesis	μ_{MAX}=0.167d^{-1} K_S=5.6gCOD/m^3 Y=0.026gVSS/gCOD
hydrogenotrophic methanogenesis	μ_{MAX}=0.695d^{-1} K_S=0.13gCOD/m^3 Y=0.018gVSS/gCOD
K_S= saturation (half velocity) concentration *K_H= hydrolysis constant* *K_I= inhibition constant* *μ_{MAX}= maximum reaction velocity* *Y= biomass yield coefficient*	

The model allows the estimation of the produced gases namely methane *(N_{CH4}),* carbon dioxide *(N_{CO2}),* and hydrogen *(N_{H2}),* with the last however being at minor quantities. Methane is assumed to be immediately transferred to the gas phase because of its low solubility, while carbon dioxide is partly dissolved to the liquid. To calculate the biogas that is finally released, we assume that produced gas and liquid are in quasi-stationary equilibrium, and that CO_2 is then distributed in the two phases according to Henry's law:

$$C_{CO2} = P_{CO2} / H_{CO2} \quad (12)$$

where C_{CO2} is the concentration of unionized carbon dioxide in the liquid (mol/L), P_{CO2} is the partial pressure of carbon dioxide in the biogas released (atm) and H_{CO2}=45.5L-atm/mol is the Henry constant for this gas (Merkel and Krauth, 1999). Biogas released is then approximated by the sum $N_{CH4} + N_{CO2,G}$, where the part of CO_2 that follows the gas phase $N_{CO2,G}$, is easily estimated as the solution of the following second degree equation:

$$N_{CO2,G} = N_{CO2} - \frac{Ka1+[H^+]}{[H^+]} \cdot \frac{P\, V_M\, N_L\, N_{CO2,G}}{H_{CO2}\,(N_{CO2,G} + N_{CH4})} \quad (13)$$

where P is the total pressure of the gas phase (atm), V_M is the molar volume (22.4 L/mole), N_L is the liquid flow rate (L/d), $Ka1$ is the first stage dissociation constant of carbonic acid ($pKa1=6.31$ *for* 35^oC) and $[H^+]$ is the hydrogen ion concentration (mol/L).

3 Application of the model

3.1 Validation of the model

For the evaluation of the model we applied it to reproduce biogas production data of whey/manure codigestion, coming from the pilot plant of T.E.I. of Athens. This plant has a continuously stirred tank reactor with an effective capacity of 100L. In the beginning, the plant was semi-continuously fed with poultry manure. When steady conditions prevailed, cheese whey was stepwise added to the feed, substituting equivalent quantity of manure in a way that COD in the feed, hydraulic retention time and hence organic loading rate remained unchanged (95 g-COD/L, 18 days and 5.2 g-COD/(L_R-d), correspondingly).

The characteristics of the two wastes are presented in table 2. Whey was added up to a fraction of 0.40 by COD (whey contributed by 40% to the COD of the feed), and feeding continued at this proportion until new steady conditions established.

The model was applied to simulate the transition from the initial conditions –when manure was only treated- to the new equilibrium conditions, when whey was also included in the feed at the fraction of 0.40. We realized that the model was overestimating biogas production. In order to avoid parameters adaptation as a whole, we only modified hydrolysis rates, based on the fact that concentration of VFA

inhibits hydrolysis. Indeed, volatile acids were at a quite high level in the reactor, ranging from 5 g/L (as acetic acid) up to 6 g/L, with the values being falling as co-treatment was proceeding (fig. 1).

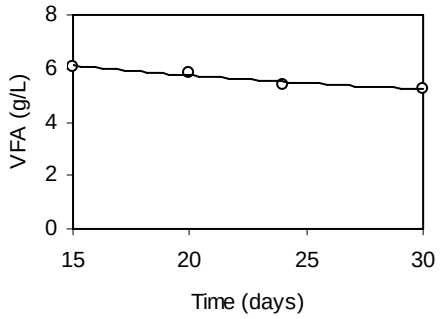

Fig. 1. Variation of VFA in the reactor. Whey was added on day 8 and reached its higher fraction of 0.4 on day 24.

Table 2. Specifications of Poultry Manure and Cheese Whey

Component	Manure	Whey
pH (at 22°C)	7.4	3.5
Total Solids, % w/w	6.3	7.8
Volatile Solids, % w/w	3.7	4.8
COD, g-O_2/l	103.6	74.9
Ash, % w/w	2.4	2.8
Ammonia Nitrogen, g/l-N	5.55	0.06
Total Nitrogen, g/l N	6.81	1.02
Alkalinity, g/l	22.6	0
Proteins, % w/w	0.8	0.6
Oil and grease, % w/w	2.7	0.7
Carbohydrates, % w/w	0.3	3.6

Angelidaki et.al. (1993) has suggested a non competitive inhibition fraction, in the form:

$$K_H = K_{H,O} \frac{K_i}{\Sigma VFA + K_i} \quad (14)$$

where $K_{H,O}$ is the non inhibited hydrolysis rate, ΣVFA is the sum of volatile acids (acetate, propionate and butyrate, taken on a molar basis and expressed as acetate in g/L) and Ki is the inhibition constant (g-VFA/L). Applying parameter identification only for this constant we found for our experiments Ki=11 g/L. The corresponding estimations of the model are now shown in fig. 2 together with the actual data.

From fig.2 becomes apparent that the model reproduces quite satisfactorily the real data by applying calibration only for the hydrolysis inhibition constant and introducing already suggested values for all other parameters. Although the model predicts the significant increase in the production, there are still some discrepancies from the real data:

- There is some overestimation of production when manure was only treated
- The model predicts lower increase of biogas production when whey is added to the feed (+40L/d instead of the actual +70L/d).
- The model estimates a very quick response for the system, which wasn't the case.

The above discrepancies probably reveal that there was some kind of inhibition when manure was only treated. This inhibition seems that was slowly alleviated by the stepwise replacement in the feed a part of manure with equivalent quantity of whey.

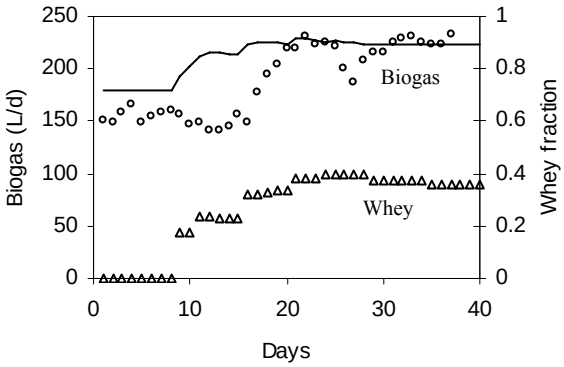

Fig.2. Experimental biogas yield compared to model, as a function of time and whey fraction. Symbols: experimental values, line: model prediction (the fraction in the right axis is expressed in whey participation in the COD of the feed).

A well known parameter that is quite often responsible for inhibition in manure digestion is ammonia (e.g. De Baere et al., 1984) that causes increase of VFA and restricts methanogenesis. Indeed, in our experiments we realized that ammonia nitrogen was at a high concentration in the manure but not in the whey (table 1). Furthermore, VFA were indeed quite high and started dropping when manure were diluted with whey (fig. 1). For this reasons we further investigate ammonia inhibition in poultry manure digestion, including the relevant equilibrium in the model.

3.2 Ammonia inhibition

Ammonia inhibition is quite probable when processing manure, especially of pig or poultry

origin. High contents of free ammonia inhibit aceticlastic methanogens, resulting to increased concentration of acetic and other volatile acids. This fact results to lower methane production but does also decrease pH in the reactor. Lower pH however limits the available free ammonia and in this way the problem seems to be alleviated rather than accelerated. In general ammonia inhibition depends on ammonia content, pH, temperature and if biomass is acclimated to ammonia or not.

Ammonia nitrogen comes to the reactor with the feed, and leaves reactor with the effluent. Ammonia is produced in the reactor due to the degradation of proteins and at the same time is consumed by the bacteria for their growth. According to the above, ammonia balance gets the form:

$$\frac{D[NH_3]}{dt} = D\cdot(NH_3\text{-}NH_{3,F}) + \frac{R_{protein}}{160} - \frac{\Sigma(\mu i\ Ci)}{113} \quad (15)$$

where the left term is the time derivative of total ammonia concentration NH_3 (in mmole/L) in the reactor, D is the dilution rate (d^{-1}), $NH_{3,F}$ is the ammonia concentration in the feed (mmole/L), $R_{protein}$ is the protein hydrolysis rate (mg-COD/d-L), μi are the bacteria growth rates (d^{-1}) and Ci the corresponding bacteria concentrations (mg-VSS/L) while the sum Σ is taken for all bacteria populations. The factor 160 stands for protein mg-COD/mmole and the factor 113 is the equivalent molecular weight of proteins (for the bacteria) expressed here in mg/mmole. Free ammonia is further calculated from total ammonia taking into consideration pH and ammonium dissociation constant (e.g. pKa=8.54 for 35^{o}C). Free ammonia non-competitive inhibition is assumed for the methanogens growth, with constant Ki=0.26 g/L (Angelidaki et al., 1993).

The results of the model with the consideration of free ammonia inhibition are shown in fig. 3. Now the model estimates more accurately the high increase in production after the partial replacement of manure with whey. Moreover the model estimates a slower response to the introduction of whey, in agreement with the correspondingly slow dilution of ammonia in the reactor (total ammonia concentration is also depicted in fig. 3).

4 Codigestion of whey with manure

After its validation, the model can be applied to draw some conclusions concerning the operation of a potential whey/manure co-digesting unit. In fig. 4 and 5 we present the variation of production from such a unit (as estimated by the model), as a response to change of various feed characteristics or operating conditions.

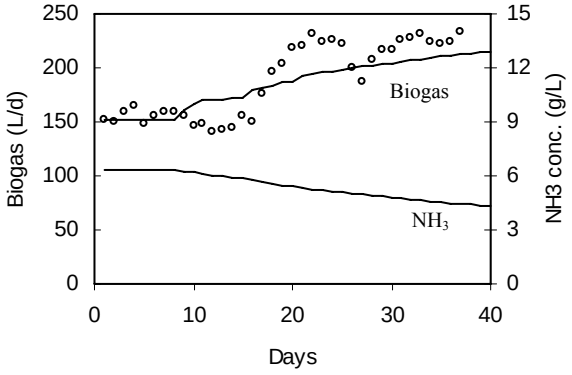

Fig.3. Experimental biogas yield compared to model, when ammonia inhibition is considered. Symbols: experimental values, lines: model predictions.

In fig. 4 the effect of whey fraction in the feed is presented. Biogas production increases with increasing whey fraction. However, this increase is almost equally due to the higher methane and carbon dioxide production rates, which results to a slight lowering of methane fraction in the biogas.

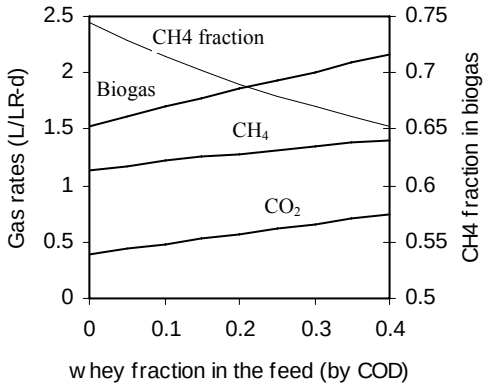

Fig. 4. Effect of cheese whey fraction to gas production, when codigested with poultry manure.

Fig. 5 presents the effect of dilution and reactor temperature to the biogas production, for the cases where (i) no whey is added and (ii) whey is added to the feed in a fraction of 0.4 (by COD). For all cases, increase in the values of the selected parameters lead to higher production. Dilution seems to be the same critical with temperature when co-treatment is applied. This is not the case however when manure is treated alone as dilution slightly affects

production, while, washout happens when dilution increases by 20%, a problem that seems that can be avoided when whey is co-digested.

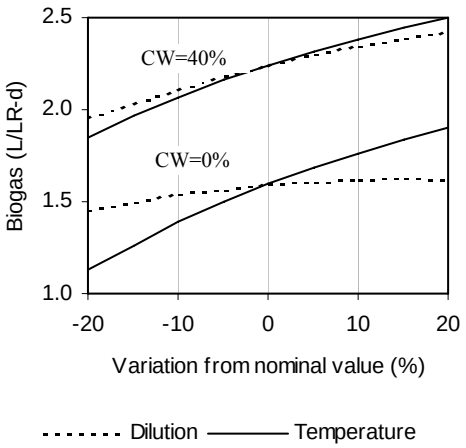

Fig. 5. Effect of dilution and temperature to biogas production, when poultry manure is treated alone (CW=0%) or codigested with whey (CW=40%)

5 Conclusion

A model was developed for the simulation of codigestion of cheese whey with poultry manure, taking into consideration the detailed composition of each waste and the various biochemical processes.

For the solution of the model, a fully implicit finite difference scheme was applied, keeping only the microbial growth rates at an explicit form. This scheme proved to be stable, under condition however (restricted time step). It was also proved to be very sensitive to the initial conditions assumed.

The model was validated according to production data from a pilot plant. It was proved that codigestion of manure with whey leads to higher biogas production for the same organic load. This was justified by the higher biodegradability of whey (includes readily biodegradable polysaccharoses instead of lipids included in the manure) and the practical absence of ammonia in whey, a fact that alleviates ammonia inhibition that usually prevails when processing manure alone.

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