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VOLUMES RATIO OPTIMIZATION IN A CASCADE ANAEROBIC DIGESTION SYSTEM PRODUCING HYDROGEN AND METHANE

Abstract: As focus of humans has turned to renewable energy, the role of anaerobic digestion has started to become economically viable. Reducing the volume of agro-wastes for the generation of gaseous and liquid fractions with energy carriers and valuable products is an enormous challenge. A two-stage anaerobic digestion process consisting of hydrogenic stage followed by methanogenic stage was studied in a laboratory scale. Five simple nonlinear models of this continuous cascade process were studied in order to determine the optimal ratio of working volumes of bioreactors, in view of maximising energy production. This ratio was reported for all adopted models. The optimal ratio (maximal energy production criterion) depends of the adopted mathematical model. Static characteristics of both bioreactors were obtained using *Symbolic* toolbox of *Matlab*. Numerical experiments concerning dynamics of the main variables of both bioreactors for these models using *Simulink* of *Matlab* are performed for different step changes of the dilution rate of the first bioreactor, together with the influence of the substrate (acetate) inhibition for one of the models. The value of the constant of inhibition plays an important role on the admissible interval of the dilution rate. The developed idea could serve for optimally designed experiments of anaerobic digestion for production of hydrogen and methane from lignocelluloses wastes (wheat straw) in two phase process.

Keywords: anaerobic digestion, two-stage process, mathematical modelling, static characteristics, maximal energy production

Introduction

Anaerobic digestion (AD) of organic wastes is a very attractive biotechnology mainly in the field of renewable energy sources and biofuels. This approach is very useful for remediation of highly polluted with organics waste waters and municipal effluents. It is known that more than 95 % of the working industrial biogas plants operate with the so called continuously stirred tank bioreactors. In this case the effluent organics is 3-4 times lower than the influent one. AD is able to synchronise human activities with natural cycles. Digestion of organic matter by microorganisms to produce energy and an organic by-product - digestate with possible use in agriculture appears as an effective and low-cost procedure. In traditional AD, hydrogen (H_2) is not detected as it is consumed immediately in the production of methane (CH_4) and carbon dioxide (CO_2) [1, 2]. On the other hand, H_2 can be produced separately by engineering the process conditions. Recently, the interest in H_2 production through AD also known as dark fermentative H_2 production, has increased [3-5]. The main limitation of dark fermentative H_2 production is the rather low energy

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recovery. In order to completely utilise the organic acids produced during dark fermentation and improve the overall energy conversion efficiency a two-stage AD (TSAD) concept consisting of hydrogenic process, followed by methanogenic process has been suggested [2, 4, 5]. The bottle-neck problems occur in the first stage (production of hydrogen) of the TSAD process. In the fermentation process mixed anaerobic and facultative anaerobic bacterial populations are involved and various metabolic pathways simultaneously act during H_2 production, revealing a complexity in action [5]. The main aspects of TSAD have been confirmed with experimental tests, either in batch or in continuous modes, using two feeds representative of organic refuses [6]. Different bioreactors were used as hydrogen or methane production reactors in TSAD. In the known literature more of the TSAD processes are operated manually and the ratio of working volume of CSTR bioreactors is not discussed. In some reports a ratio of ten is accepted without comments. According to Dareioti and Kornaros [7] a TSAD system consisting of two CSTRs operating at mesophilic conditions was used to investigate the effect of hydraulic retention time (the reciprocal value of the dilution rate) on hydrogen and methane production. The ratio of working volumes of bioreactors is equal of eight (without comments). Cavinato et al. [8] performed optimization of TSAD with separately collected municipality biowaste in a pilot scale CSTRs at thermophilic regime using recirculation of the digestate of the second BR to maintain the pH in the first BR at the optimal value. The ratio of working volumes of bioreactors is equal of 3.8. Optimal loading rate is obtained providing maximum H_2 and CH_4 productions in TSAD of cassava wastewaters using specific thermophilic bioreactors and constant recycling ratio of 1:1 with automatic control of pH in the hydrogenic bioreactor in the report of Intanoo et al. [9]. The ratio of working volumes of both bioreactors is equal of 6 (without explanation). In the work of Schievano et al. [10] both bio-hydrogen and bio-methane productions are optimised in thermophilic bioreactors regarding two operating parameters (organic loading rate and dilution rate), however, the first bioreactor is running in semi-continuous and the second - in batch operation mode, because working volumes of both bioreactors are equal. The first review article by Khan et al. [11] combines the optimization approaches for three possible products from AD - methane, hydrogen and volatile fatty acids (VFA), taking into account different process parameters and types of BR, including acidogenesis and methanogenesis separation in two different BRs. However, the ratio of working volumes of the bioreactors is not included and discussed.

Biogas production is growing in the European energy market and in a few decades it will offer an economical alternative for the production of bio energy [5]. One of the parameters to be optimised for TSAD is the ratio of the working volumes of both bioreactors used. A number of models describing the fermentative hydrogen production and the AD for methane production are known but only few models of TSAD processes are offered [12]. Although modelling of two-stage anaerobic digestion using the IWA Anaerobic Digestion Model No 1 (ADM1) is presented by Blumensaat and Keller [13], the described AD process is not real TSAD process because methane is obtained from both bioreactors. The volumes of the bioreactors are presented separately but without discussing the ratio between them. Previous experimental studies of co-digestion of mixtures of milk whey and waste activated sludge in a TSAD process and modelling of this processes have been conveyed *by us*, where methane is obtained from both bioreactors as well as extremum-seeking control design and application for anaerobic digestion processes [14].

The aim of this study is to analyse some mathematical models of a continuous process of TSAD with production of hydrogen and methane in a cascade of two CSTRs, in order to find a solution of the very important problem for practice - optimization of the ratio of the working volumes of both bioreactors in view of maximising the energy production. To our knowledge this is the first attempt to theoretically investigate this problem.

Methods

The application of a TSAD process, including two bioreactors for sequential H_2 and CH_4 production in CSTRs has been proposed for better process performance and higher energy yields as compared to the traditional one-stage CH_4 production process. Laboratory installation was used (Fig. 1).

Fig. 1. Two-stage process of AD with production of hydrogen and methane

By definition for: CSTRs $D_1 = \frac{F}{V_1}$ and $D_2 = \frac{F}{V_2}$. After some transformations it was obtained that: $K = \frac{V_2}{V_1} = \frac{D_1}{D_2}$. In the known literature there are no discussions and solutions how to obtain an optimal value of the coefficient K . The static input-output characteristics both for hydrogen $Q_{H_2} = f_1(D_1)$ and for methane $Q_{CH_4} = f_2(D_2)$ flow rates present extrema (maxima) in the admissible range of the control input (D_1) for different values of the main perturbation - S_0^{in} [12, 14, 15].

The new idea for calculating the optimal ratio of the working volumes of both bioreactors is based on the possibility to assure operating of both bioreactors in the points of maximal biogas (hydrogen and methane) production: $K_{\text{opt}} = \frac{V_2}{V_1} = \frac{D_{1\text{max}}}{D_{2\text{max}}}$. In this case K is optimal in the sense of maximal energy production ($Q_{H_2} + Q_{CH_4} = \text{Max}$).

Results and discussion

Modelling of the processes for simultaneous production of H₂ and CH₄

The application of a TSAD process for sequential H₂ and CH₄ production in CSTRs has been proposed as a promising technology for better process performance and reaching higher energy yields as compared to the traditional one-stage CH₄ production process. It is known that in the two-stage H₂+CH₄ system with CSTRs the energy yields are 20-40 % higher compared to the traditional one-stage CH₄ production process [4, 5]. Experimental studies in a laboratory scale on AD of lignocellulosic waste (wheat straw) in single and two-stage processes with production of hydrogen through the acidogenic phase and of methane through the methanogenic phase was studied. As a result, the total amount of energy that is produced in the single-stage methanogenic process is 34 % less compared to a two-staged one. This difference comes from both - hydrogen released - about 17 % together with the increased amount of methane - about 13 % [16]. In the TSAD system, relatively fast growing acidogens and H₂-producing microorganisms are developed in the first-stage hydrogenic bioreactor (BR₁) with working volume V₁ and pH in the interval 5.0-5.5, operating with dilution rate D₁. They are involved in the production of acetate, propionate, butyrate and H₂ (acidogenesis) and acetate consuming methanogens are eliminated. On the other hand, the slow growing acetogens and methanogens are developed in the second-stage methanogenic bioreactor (BR₂) with working volume V₂ and pH in the interval 6.5-8.5, operating with dilution rate D₂ in which the produced propionate and butyrate are further converted to acetate (acetogenesis) and after that to CH₄ and CO₂ (methanogenesis).

The object of our interest was five balance models of the process in CSTRs consisting of some ODEs and algebraic equations as follows:

Equations (1) and (2) present balances of the substrates (S₀ and S₁) - for example cellulose and cellobiose. Equation (3) describes the dynamics of the biomass (for ex. *Clostridium thermocellum*) concentration (X₁), equation (4) - dynamics of the product (acetate) formation (Ac₁) and the algebraic equation (5) - the flow rate of the hydrogen in the gas phase in BR₁. For the specific growth rate of the biomass a Monod type function was adopted (5). Model of the processes without hydrolysis were called MODEL1; Model of the processes with hydrolysis including acetate as an intermediate product, called MODEL2:

- BR₁:

$$\frac{dS_0}{dt} = -D_1 S_0 - \beta X_1 S_0 + D_1 Y_p S_0^{\text{in}} \quad (1)$$

$$\frac{dS_1}{dt} = -D_1 S_1 + \beta X_1 S_0 - \frac{1}{Y_1} \mu_1 X_1 \quad (2)$$

$$\frac{dX_1}{dt} = \mu_1 X_1 - D_1 X_1 \quad (3)$$

$$\frac{dAc_1}{dt} = \frac{1}{Y_2} \mu_1 X_1 - D_1 Ac_1 \quad (4)$$

$$Q_{H_2} = Y_{H_2} \mu_1 X_1 \quad (5)$$

$$\mu_1 = \frac{\mu_{1\max} S_1}{K_{S1} + S_1} \quad (6)$$

- BR₂:

$$\frac{dX_2}{dt} = \mu_2 X_2 - D_2 X_2 \quad (7)$$

$$\frac{dAc_2}{dt} = -\frac{1}{Y_3} \mu_2 X_2 + D_2 (Ac_1 - Ac_2) \quad (8)$$

$$Q_{CH_4} = Y_{CH_4} \mu_2 X_2 \quad (9)$$

$$\mu_2 = \frac{\mu_{2\max} Ac_2}{K_{S2} + Ac_2} \quad (10)$$

Model of the processes with hydrolysis including acetate as an intermediate product and substrate inhibition is called MODEL3. This model is the same as MODEL2 with the unique difference in the specific growth rate of methanogenic bacteria equation for BR₂, including substrate inhibition [17]:

$$\mu_2 = \frac{\mu_{2\max} Ac_2}{K_{S2} + Ac_2 + Ac_2^2 / K_i} \quad (11)$$

Model of the processes with hydrolysis including acetate and propionate as intermediate products is called MODEL4:

- BR₁:

$$\frac{dS_0}{dt} = -D_1 S_0 - \beta X_1 S_0 + D_1 Y_p S_0^{\text{in}} \quad (12)$$

$$\frac{dS_1}{dt} = -D_1 S_1 + \beta X_1 S_0 - \frac{\mu_1 X_1}{Y_1} \quad (13)$$

$$\frac{dX_1}{dt} = \mu_1 X_1 - D_1 X_1 \quad (14)$$

$$\frac{dPr_1}{dt} = \frac{\mu_1 X_1}{Y_{Pr1}} - D_1 Pr_1 \quad (15)$$

$$\frac{dAc_1}{dt} = \frac{\mu_1 X_1}{Y_{Ac1}} - D_1 Ac_1 \quad (16)$$

$$Q_{H_2} = Y_{H_2} \mu_1 X_1 \quad (17)$$

$$\mu_1 = \frac{\mu_{1\max} S_1}{K_{S1} + S_1} \quad (18)$$

- BR₂:

$$\frac{dX_{Pr}}{dt} = \mu_{Pr} X_{Pr} - D_2 X_{Pr} \quad (19)$$

$$\frac{dPr_2}{dt} = -\frac{\mu_{Pr} X_{Pr}}{Y_{Pr2}} + D_2 (Pr_1 - Pr_2) \quad (20)$$

$$\frac{dX_{Ac}}{dt} = \mu_{Ac} X_{Ac} - D_2 X_{Ac} \quad (21)$$

$$\frac{dAc_2}{dt} = -\frac{\mu_{Ac} X_{Ac}}{Y_{Ac2}} + \frac{\mu_{Pr} X_{Pr}}{Y_{Pr2}} + D_2 (Ac_1 - Ac_2) \quad (22)$$

$$Q_{CH_4} = Y_{CH_4} \mu_{Ac} X_{Ac} \quad (23)$$

$$\mu_{Pr} = \frac{\mu_{Pr \max} Pr_2}{K_{SPr} + Pr_2} \quad (24)$$

$$\mu_{Ac} = \frac{\mu_{Ac \max} Ac_2}{K_{SAc} + Ac_2} \quad (25)$$

Models 2, 3 and 4 are developed from a methodological point of view - to prove that the adopted approach for obtaining the optimal ratio of working volumes is admissible for different kind of models.

Model of the processes with hydrolysis including acetate, propionate and butyrate as intermediate products [18] is called MODEL5. The definitions of the model variables and parameters in the equations (1)-(25) are given in Tables 1 and 2.

Table 1

Model variables

Notation	Definition
t	Time [h]
D_1	Dilution rate for BR ₁ [h ⁻¹]
$D_{1 \max}$	Value of D_1 corresponding of $Q_{H_{2 \max}}$
$D_{1 \text{sub}}$	Admissible value of D_1 (without wash-out of acidogenic bacteria)
D_2	Dilution rate for BR ₂ [h ⁻¹]
$D_{2 \max}$	Value of D_2 corresponding of $Q_{CH_{4 \max}}$
$D_{2 \text{sub}}$	Admissible value of D_2 (without wash-out of methanogenic bacteria)
S_0^{in}	Inlet cellulose concentration in BR ₁ [g/L]
S_0	Cellulose concentration [g/L]
S_1	Cellobiose substrate concentration [g/L]
X_1	Acidogenic bacteria concentration [g/L]
X_2	Methanogenic bacteria concentration [g/L]
X_{Pr}	Propionate degrading bacteria concentration [g/L]
X_{Ac}	Methanogenic bacteria concentration [g/L]
μ_1	Specific growth rate for acidogenic bacteria [h ⁻¹]
μ_2	Specific growth rate for methanogenic bacteria [h ⁻¹]
μ_{Pr}	Specific growth rate for propionate degrading bacteria [h ⁻¹]
μ_{Ac}	Specific growth rate for methanogenic bacteria [h ⁻¹]

VFA	Volatile fatty acids concentration
Pr_1, Pr_2	Propionate concentration [g/L]
Ac_1, Ac_2	Acetate concentration [g/L]
Ac_{1max}	The value of Ac_1 , corresponding of D_{1max} in BR ₁
Q_{H_2}	Hydrogen flow rate [L/h]
$Q_{H_{2max}}$	Maximal value of Q_{H_2}
Q_{CH_4}	Methane flow rate [L/h]
$Q_{CH_{4max}}$	Maximal value of Q_{CH_4}
V_1, V_2	Working volumes of BR ₁ and BR ₂ [L]

Table 2

Model parameters

Notation	Value	Definition
μ_{1max}	0.568	Maximum specific growth rate for acidogenic bacteria [h ⁻¹]
μ_{2max}	0.0083	Maximum specific growth rate for methanogenic bacteria [h ⁻¹]
μ_{Prmax}	0.05	Maximum specific growth rate for propionate degrading bacteria [h ⁻¹]
μ_{Acmax}	0.025	Maximum specific growth rate for methanogenic bacteria [h ⁻¹]
K_{S1}	3.914	Saturation coefficient for acidogenic bacteria [g/L]
K_{S2}	0.22	Saturation coefficient for acetogenic bacteria [g/L]
K_{SPr}	0.22	Saturation coefficient for propionate [g/L]
K_{SAc}	0.8	Saturation coefficient for acetate [g/L]
K_i	10	Inhibition constant [g/L]
K_i^{inf}	-	A lower bound of K_i
β	1	Coefficient of biodegradability [L/(g·h)]
Y_p	1	Coefficient [-]
Y_1	0.08	Yield coefficient for acidogenic bacteria [-]
Y_2	1	Yield coefficient for acetogenic bacteria [-]
Y_3	0.24	Yield coefficient for methanogenic bacteria [-]
Y_{Pr1}	2.1	Yield coefficient for propionate [-]
Y_{Ac1}	1.1	Yield coefficient for acetate [-]
Y_{Pr2}	1.5	Yield coefficient for propionate [-]
Y_{Ac2}	0.5	Yield coefficient for acetate [-]
Y_{H_2}	1	Yield coefficient for hydrogen [L/g]
Y_{CH_4}	142	Yield coefficient for methane [L/g]
K	-	Ratio of working volumes of bioreactors [-]
K_{opt}	-	Optimal ratio of working volumes of bioreactors [-]

Numerical experiments concerning dynamics of the main variables of both bioreactors for all above presented models using *Simulink* of *Matlab* are performed for different step changes of the control variable D_1 (D_2). Some results concerning the dynamics of the flow rates of hydrogen Q_{H_2} and methane Q_{CH_4} for step changes of the control variable D_1 (D_2)

are presented in Table 3 using MODEL2 ($K = 56.4$) are shown on Figures 2 and 3. Figure 2 for BR_1 is plotted with 20 times shorter periods for visualization.

Fig. 2. Dynamics of the hydrogen flow rate Q_{H_2} (BR_1) for step changes of the control variable D_1 presented in Table 3

Fig. 3. Dynamics of the methane flow rate Q_{CH_4} (BR_2) for step changes of the control variable D_2 presented in Table 3

The simulation results from Figures 2 and 3 illustrate the model validity.

Table 3

 Step changes of D_1 ($D_2 = D_1/67$)

Hour	0-149(2999)	150(3000)-299(5999)	300(6000)-450(9000)
D_1 [h^{-1}]	0.15	0.2	0.1

Static characteristics of BR₁ and BR₂

Transforming the equations of the balance models using *Symbolic* toolbox of *Matlab*, some algebraic equations called static characteristics of both bioreactors were obtained. They represent dependencies of the main process variables from the dilution rates. The static characteristics for MODEL1 and for MODEL5 are shown in Chorukova and Simeonov [12].

- Static characteristics for MODEL2, BR₁

$$S_0 = S_0(D_1, S_0^{\text{in}}) = \frac{P_1 - P_2}{Y_1} \quad (26)$$

$$S_1 = S_1(D_1) = \frac{K_{S1}D_1}{\mu_{1\max} - D_1} \quad (27)$$

$$X_1 = X_1(D_1, S_0^{\text{in}}) = P_1 + P_2 \quad (28)$$

$$Ac_1 = Ac_1(D_1, S_0^{\text{in}}) = \frac{P_1 + P_2}{Y_2} \quad (29)$$

$$Q_{H_2} = Q_{H_2}(D_1, S_0^{\text{in}}) = Y_{H_2}D_1(P_1 + P_2) \quad (30)$$

$$P_1 = \frac{\mu_{1\max} S_0^{\text{in}} Y_1 Y_p - K_{S1} Y_1 D_1 - S_0^{\text{in}} Y_1 Y_p D_1}{2(\mu_{1\max} - D_1)} \quad (31)$$

$$P_2 = \frac{D_1^2 - \mu_{1\max} D_1 + \sqrt{P_3}}{2\beta(\mu_{1\max} - D_1)} \quad (32)$$

$$\begin{aligned} P_3 = & D_1^4 - 2\mu_{1\max} D_1^3 + 2\beta K_{S1} Y_1 D_1^3 - 2\beta S_0^{\text{in}} Y_1 Y_p D_1^3 + \beta^2 K_{S1}^2 Y_1^2 D_1^2 + \\ & + 2\beta^2 K_{S1} S_0^{\text{in}} Y_1^2 Y_p D_1^2 + \beta^2 S_0^{\text{in}2} Y_1^2 Y_p^2 D_1^2 - 2\beta K_{S1} \mu_{1\max} Y_1 D_1^2 + \\ & + 4\beta \mu_{1\max} S_0^{\text{in}} Y_1 Y_p D_1^2 + \mu_{1\max}^2 D_1^2 - 2\beta^2 K_{S1} \mu_{1\max} S_0^{\text{in}} Y_1^2 Y_p D_1 - \\ & - 2\beta^2 \mu_{1\max} S_0^{\text{in}2} Y_1^2 Y_p^2 D_1 - 2\beta \mu_{1\max}^2 S_0^{\text{in}} Y_1 Y_p D_1 + \beta^2 \mu_{1\max}^2 S_0^{\text{in}2} Y_1^2 Y_p^2 \end{aligned} \quad (33)$$

- Static characteristics for MODEL2, BR₂ (the same as for MODEL1, BR₂):

$$Ac_2 = Ac_2(D_2) = \frac{D_2 K_{S2}}{\mu_{2\max} - D_2} \quad (34)$$

$$X_2 = X_2(D_1, S_0^{\text{in}}, D_2) = Y_3 \left(Ac_1 - \frac{D_2 K_{S2}}{\mu_{2\max} - D_2} \right) \quad (35)$$

$$Q_{CH_4} = Q_{CH_4}(D_1, S_0^{\text{in}}, D_2) = Y_3 Y_{CH_4} D_2 \left(Ac_1 - \frac{D_2 K_{S2}}{\mu_{2\max} - D_2} \right) \quad (36)$$

- Static characteristics for MODEL3, BR₁ are the same as for MODEL2, BR₁.
- Static characteristics for MODEL3, BR₂ (with acetate inhibition on the methanogenic bacterial population):

$$Ac_2 = Ac_2(D_2) = \frac{P_4 - D_2 K_i + K_i \mu_{2\max}}{2D_2} \quad (37)$$

$$X_2 = X_2(D_1, S_0^{\text{in}}, D_2) = \frac{-Y_3 P_4 + 2D_2(P_1 + P_2)/Y_2 + D_2 K_i - K_i \mu_{2\max}}{2D_2} \quad (38)$$

$$Q_{CH_4} = Q_{CH_4}(D_1, S_0^{\text{in}}, D_2) = \frac{-Y_3 Y_{CH_4} P_4 + 2D_2(P_1 + P_2)/Y_2 + D_2 K_i - K_i \mu_{2\max}}{2} \quad (39)$$

$$P_4 = \sqrt{K_i(D_2^2 K_i - 4D_2^2 K_{S2} + K_i \mu_{2\max}^2 - 2D_2 K_i \mu_{2\max})} \quad (40)$$

- Static characteristics for MODEL4, BR₁ are the same as for MODEL2, BR₁, with the only difference for:

$$Pr_1 = Pr_1(D_1, S_0^{\text{in}}) = \frac{P_1 + P_2}{Y_{Pr}} \quad (41)$$

$$Ac_1 = Ac_1(D_1, S_0^{\text{in}}) = \frac{P_1 + P_2}{Y_{Ac_1}} \quad (42)$$

- Static characteristics for MODEL4, BR₂:

$$X_{Pr} = X_{Pr}(D_2, Pr_1) = Y_{Pr_2} \left(Pr_1 - \frac{D_2 K_{SPr}}{\mu_{Pr\max} - D_2} \right) \quad (43)$$

$$Pr_2 = Pr_2(D_2) = \frac{D_2 K_{SPr}}{\mu_{Pr\max} - D_2} \quad (44)$$

$$Ac_2 = Ac_2(D_2) = \frac{D_2 K_{SAc}}{\mu_{Ac\max} - D_2} \quad (45)$$

$$X_{Ac} = X_{Ac}(D_2, Pr_1, Ac_1) = \frac{Y_{Ac_2} P_5}{(\mu_{Pr\max} - D_2)(\mu_{Ac\max} - D_2)} \quad (46)$$

$$Q_{CH_4} = Q_{CH_4}(D_2, Pr_1, Ac_1) = \frac{Y_{Ac_2} Y_{CH_4} D_2 P_5}{(\mu_{Pr\max} - D_2)(\mu_{Ac\max} - D_2)} \quad (47)$$

$$\begin{aligned} P_5 = & Pr_1 D_2^2 + Ac_1 D_2^2 + K_{SPr} D_2^2 + K_{SAc} D_2^2 - Pr_1 \mu_{Pr\max} D_2 - \\ & - Pr_1 \mu_{Ac\max} D_2 - Ac_1 \mu_{Pr\max} D_2 - Ac_1 \mu_{Ac\max} D_2 + Pr_1 \mu_{Pr\max} \mu_{Ac\max} + \\ & + Ac_1 \mu_{Pr\max} \mu_{Ac\max} - K_{SPr} \mu_{Ac\max} D_2 - K_{SAc} \mu_{Pr\max} D_2 \end{aligned} \quad (48)$$

- Static characteristics $Q_{H_2} = f(D_1)$ and $Q_{CH_4} = f(D_2)$ for different values of S_0^{in} in the case of MODEL5 [19] are presented on Figure 4. The concentration of influent organic matter is taken as the main external disturbance, which is reflected in the models. Its change leads to a shift of the corresponding static characteristics, without changing their nature, but of course the value of the maximum also changes.

a)

b)

Fig. 4. Static characteristics for different values of S_0^{in} in the case of MODEL5: a) hydrogen yield in dependence of dilution rate in BR₁ and b) methane yield in dependence of dilution rate in BR₂

Analysing static characteristics it is evident that all static characteristics are nonlinear. Most static characteristics are depending from inlet substrate concentration in BR_1 (S_0^{in}). Only the static characteristics of the hydrogen flow rate and methane flow rate presents extremums (maxima) for both of them in the admissible range of the control input (D_1) for different values of the main perturbation - S_0^{in} . That is a good possibility for realization of extremum-seeking control algorithms [16]. It is known that reactions rates in BR_1 are much faster than these in BR_2 . To optimise the functioning of the two-stage process in continuous operation mode, the working volume of BR_2 must be bigger than that of BR_1 . *But how many times?* We could propose the following idea: We suppose that BR_1 is working in the optimal point for maximising the hydrogen production and BR_2 , as well, is working in the optimal point for maximising the methane production. To reach this situation it is sufficiently that:

$$K = \frac{V_2}{V_1} = \frac{D_{1max}}{D_{2max}} \quad (49)$$

Calculating the coefficient K was done as follows: First, the static characteristics of Q_{H_2} and Q_{CH_4} for different values of S_0^{in} and varying in appropriate intervals D_1 and D_2 using model parameters shown in nomenclature were calculated. After that D_{1max} and D_{2max} were taken down for corresponding $Q_{H_2}^{max}$ and $Q_{CH_4}^{max}$. Using this values K was calculated. In this case it will be possible to obtain maximum energy (maximal energy production criterion). Our studies show that the coefficient K depends on S_0^{in} . That is why the characteristic $K = f(S_0^{in})$, determining the ratio of the working volumes of the two bioreactors, was obtained using (49) for different values of S_0^{in} . For all investigated models and $S_0^{in} \in (15-35)$ g/L, characteristics $K = f(S_0^{in})$ are presented on Figure 5 and in Table 4. The optimal ratio of the working volumes of the two bioreactors is approximately the same at different values of S_0^{in} , which results from the very way of its analytical determination.

Table 4

Values of K [-]

S_0^{in}	15 [g/L]	20 [g/L]	25 [g/L]	30 [g/L]	35 [g/L]	Average
MODEL1	68.89	68.00	67.92	66.96	67.24	67.8
MODEL2	50.00	54.17	57.84	59.26	60.71	56.4
MODEL3	45.74	52.00	55.66	58.18	60.71	54.5
MODEL4	26.88	27.37	28.10	26.67	27.20	27.2
MODEL5	27.50	26.00	26.36	26.67	26.15	26.5

Fig. 5. Characteristic $K = f(S_0^{in})$ for all studies models

The initial conditions in relation to the main variables (concentrations of substrates and microorganisms) play a role only at the start of the process (as a batch process). In models of processes of continuous type, each value of the control variable D corresponds to certain values of all other variables, which are coordinates of the corresponding steady state of the process and appear to be initial values at the next change of D . The stability of these steady states had already been shown in our previous work [17]. The important point is that in the area of the admissible range of control variable, which always includes the corresponding maximum, the equilibrium states are always stable. In the area of the permissible range of the control variable, which always includes the corresponding maximum, the equilibrium states are always stable. The optimal ratio of the working volumes of the two bioreactors is approximately the same at different values of S_0^{in} , which results from the very way of its analytical determination.

Finally, for each model K may be accepted as a constant equal of the average value. A theoretical study was performed for the influence of the substrate (acetate) inhibition (MODEL 3) on the above developed idea. Obtained results show that the value of the constant of inhibition K_i plays an important role on the admissible interval of the dilution rate D_2 . The key values of the dilution rate D_2 (max and sub) as a function of the constant of inhibition for three values of S_0^{in} are shown on Figures 6-8. The conclusion from these figures is that there exists a lower bound for $K_i = K_i^{inf}$ at which $D_{2max} = D_{2sub}$ (for the existing of maxima of Q_{CH_4}). In Table 5 the calculated values of K_i^{inf} for different S_0^{in} are shown.

Table 5

Values of K_i^{inf} for different S_0^{in}

S_0^{in}	15 [g/L]	20 [g/L]	25 [g/L]	30 [g/L]	35 [g/L]
K_i^{inf}	1.1	1.9	2.9	4.1	5.4

Fig. 6. D_{2sub} and D_{2max} as a function of K_i for $S_0^{in} = 15$ g/L

Fig. 7. D_{2sub} and D_{2max} as a function of K_i for $S_0^{in} = 25$ g/L

Fig. 8. D_{2sub} and D_{2max} as a function of K_i for $S_0^{in} = 35$ g/L

As an illustration of the above presented theoretical results the curves depicting D_{2sub} and D_{2max} as a function of Ac_{1max} are presented on Figure 9. Ac_1 is the concentration of acetate in the effluent of BR_1 and in the influent of BR_2 , respectively. From equations (29) to (33) it is evident that Ac_1 is a function of S_0^{in} and D_1 . Ac_{1max} is the value corresponding of D_{1max} in BR_1 . Figure 9 illustrates that D_{2max} is in the admissible interval for all studied values of the inlet concentration of S_0^{in} .

Another conclusion from our theoretical study is that the maximal value of Q_{CH_4} in the case of existence of substrate (acetate) inhibition on the methanogenic bacterial population is lower compared to the case without inhibition.

From all cases that have been analysed it is evident that the optimal ratio (maximal energy production criterion) of the working volumes of both bioreactors depends of the adopted mathematical model. The choice of the model depends on the used substrates (wastes): in the case of simple waste (e.g. vinasses) simple models are sufficient for process description [20]. In this case the optimal ratio is characterised with high value of K , because the reactions rates in the BR_1 are very high compared to these in BR_2 . In the case of more complex substrates (sugars and proteins) more complex models are necessary and the value of K is smaller, because the reactions of hydrolysis and acidogenesis in the BR_1 are more complex and their rates are not so high compared to the first case and these in BR_2 remaining with the same rates. In the case of very complex substrates (fats and co-digestion of different wastes) much complex models are necessary and the value of K is much smaller (e.g. $K \approx 4$ as in [16]) due to existing of different complex reactions of the hydrolysis and acidogenesis in BR_1 and these in BR_2 remaining with the same rates. All models and the obtained results concern only the case of CSTRs in the TSAD processes.

Fig. 9. D_{2sub} and D_{2max} as a function of Ac_{1max} for $K_i = 10$ and $K_{S2} = 0.22$

We could not miss the environmental benefits of biogas technology including anaerobic digestion of lignocellulosic wastes for energy production [17, 21], as a valid sustainable alternative to fossil fuels, so developing appropriate models, characterising these processes is of utmost importance.

Conclusion

Simple models of the AD of organic wastes for simultaneous production of hydrogen and methane in a two-stage process, including some intermediate products, were developed and their static characteristics were theoretically obtained. A new idea for calculating the optimal ratio of the working volumes of both bioreactors (hydrogenic and methanogenic) based on the operating of both bioreactors in the points of maximal biogas (hydrogen and methane) production is proposed and illustrated with the developed simple models. The obtained results present optimal solutions of the very important problem for practice - determination of the optimal ratio (criterion - maximal energy production) of the working volumes of both bioreactors. In all cases the working volume of the hydrogenic BR_1 is much smaller than the volume of the methanogenic BR_2 . This is favourable for large-scale industrial applications where methanogenic BR is existing and investments are smaller.

The obtained input-output static characteristics for the energy carriers hydrogen and methane present maxima for both of them in the admissible range of the control inputs for different values of the main perturbation - inlet substrate concentration in first bioreactor. That is a good possibility for realization of extremum-seeking control algorithms. The optimal ratio (maximal energy production criterion) of the working volumes of both bioreactors depends of the adopted mathematical model that can be applied in real conditions for different substrates such as lignocelluloses wastes (wheat straw).

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