Static Characteristics of the Anaerobic Digestion of Organic Wastes with Production of Hydrogen and Methane, Including Substrate Inhibition Influence

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Abstract: *In this paper, static characteristics of a simple mathematical model of a two-stage anaerobic digestion (AD) process for sequential production of hydrogen (H_2) and methane (CH_4) are derived. The influence of substrate inhibition in the first and second bioreactors is considered. Different process variables are described in the considered mathematical model. The concentration of the influent organic matter is assumed to be the main external disturbance reflected in the model. The obtained input-output static characteristics for the energy carriers (H_2 and CH_4) could be used to control and optimize the subjected process.*

Keywords: *Two-stage anaerobic digestion, Mathematical model, Static characteristics, Substrate inhibition.*

Introduction

Much attention has been paid to anaerobic digestion (AD) of organic waste as an attractive alternative technology for efficient waste treatment and simultaneously production of renewable energy carriers through biogas use [6]. AD of bio wastes is the most conventional way to produce green energy and has a great potential to replace fossil fuels, needed in the increasing industrialization [5]. Anaerobic digestion is a multi-step biotechnological process with hydrogen (H_2) as a non-accumulating intermediate product. The interest in H_2 production through AD has increased during the last years. The main limitation of dark fermentative H_2 production is the rather low energy recovery. In order to completely utilize the organic acids produced during dark fermentation and improve the overall energy conversion efficiency, a two-stage AD concept, consisting of a hydrogenic process, followed by a methanogenic process has been proposed [11]. Numerous studies have been published on this topic. Many authors reported different applications of the two-stage AD with various organic substrates, and a great number of process designs [9]. Generally, two-stage anaerobic digestion has been identified as a very promising method due to the fact it allows the reduction of organic load and an increase in the overall energy conversion efficiency. The focus is on generating two gases that possess a high combustion power [7].

Nevertheless, its widespread application till now has been limited, because of the complexity of the processes, modeling, and prediction come to help. Application of suitable models makes possible the evaluation of AD process behavior and for attaining stability, accompanied by positive energy balance and low operating cost [14]. A simple AD model could capture the complexity of the process and allow sustained operation under a feedback control law [3].

The performance of any system is the ultimate decider for its application and utility. The two basic characteristics of the performance are static and dynamic. Dynamic characteristics tell us about the responses to changes in the input [4]. The process characteristics that do not vary with respect to time are called static characteristics [12].

The aim of this study is to develop and analyze some static characteristics of a continuous process of AD with a production of hydrogen and methane in a cascade of two bioreactors and estimate the influence of substrate inhibition in the first, second, and both phases.

Process description

The application of a two-stage AD process for sequential hydrogen (H_2) and methane (CH_4) production (Fig. 1) has been proposed as a promising technology for better process performance and higher energy yields as compared to the traditional one-stage CH_4 production process. In the two-stage AD system, relatively fast-growing acidogenic and hydrogen-producing microorganisms are developed during the first-stage in the hydrogenic bioreactor (BR_1 with working volume V_1) and are involved in the production of volatile fatty acids and H_2. On the other hand, the slow-growing acetogens and methanogens are developed during the second-stage in the methanogenic bioreactor (BR_2 with working volume V_2), in which the produced volatile fatty acids are further converted to CH_4 and CO_2. It is known that in the two-stage H_2+CH_4 system, the energy yields are 21-22 % more, as compared to the traditional one-stage CH_4 production process [13].

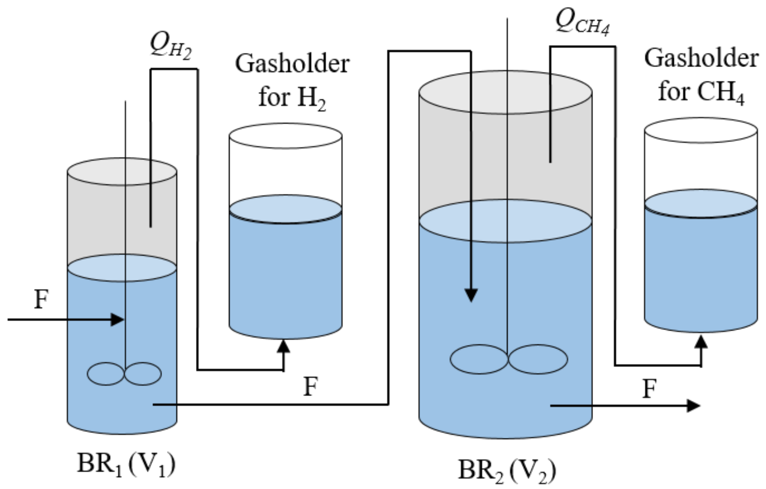

Fig. 1 The scheme of two-phases process of anaerobic digestion with a production of hydrogen and methane

Modeling of the processes for the production of H_2 and CH_4

Many mathematical models describing the whole process or some key steps have been given in the last decades. The behavior of microbial species is a major challenge for the mathematical theory of the anaerobic digestion process. Acetogenesis and hydrogenotrophic methanogenesis phases were followed with the inclusion of distinct removal rates for the species in some investigations [8].

The mathematical model of the two-stage AD process is presented by Eqs. (1)-(4), for BR_1 [2]:

$$\frac{dS_1}{dt} = -\frac{1}{Y_1}\mu_1 X_1 + D_1\left(S_1^{in} - S_1\right) \quad (1)$$

$$\frac{dX_1}{dt} = \mu_1 X_1 - D_1 X_1 \quad (2)$$

$$\frac{dAc_1}{dt} = \frac{1}{Y_2}\mu_1 X_1 - D_1 Ac_1 \quad (3)$$

$$Q_{H_2} = Y_{H_2}\mu_1 X_1, \quad (4)$$

where Eq. (1) shows the balance of the substrate (S_1); Eq. (2) describes the dynamics of the biomass concentration (X_1); Eq. (3) presents the dynamics of the product (acetate) formation (Ac_1), and Eq. (4) demonstrates the flow rate of the hydrogen Q_{H_2} in the gas phase in BR_1.

In the model Eq. (1)-(4) D_1 (h^{-1}) is the dilution rate for the first bioreactor BR_1; S_1^{in} (g/L) – inlet substrate concentration in BR_1; Y_1, Y_2, and Y_{H_2} – yield coefficients. How to predict the reactor behavior was shown in the studies of [1], who stated that it varies as a function of influent concentration and identifies the range of influent concentrations, where the reactor displays neither periodic nor bistable behavior.

The specific growth rate (μ_1) has Monod type form in the case without substrate inhibition in Eq. (5) [2]. In the case with substrate inhibition, which is the case studied in our research, it has form as Eq. (6).

$$\mu_1 = \frac{\mu_{1max} S_1}{K_{s1} + S_1} \quad (5)$$

$$\mu_1 = \frac{\mu_{1max} S_1}{K_{s1} + S_1 + S_1^2 / K_{i1}} \quad (6)$$

In Eqs. (5) and (6) μ_{1max} and K_{s1} are kinetic coefficients; K_{i1} is the inhibition constant, (g/L).

The dynamics in BR_2 are described by Eqs. (7), (8), and (9).

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

$$\frac{dAc_2}{dt} = -\frac{1}{Y_3}\mu_2 X_{2_1} - D_2(Ac_1 - Ac_2) \quad (8)$$

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

where Eq. (7) describes the dynamics of the methanogenic population with concentration (X_2); Eq. (8) presents the balance of the substrate (acetate) with concentration (S_2), and Eq. (9) shows the flow rate of the methane in the gas phase of BR_2. In the model Eqs. (7), (8), and (9) D_2 (h^{-1}) is the dilution rate for the second bioreactor BR_2, and Y_3 and Y_{CH_4} are yield coefficients.

The specific growth rate of the methanogenic population (μ_2) has Monod type form as Eq. (10) in the case without substrate inhibition. The new form developed in this study is Eq. (11). It concerns the case with substrate (acetate) inhibition:

$$\mu_2 = \frac{\mu_{2max} Ac_2}{K_{s2} + Ac_2} \tag{10}$$

$$\mu_2 = \frac{\mu_{2max} Ac_2}{K_{s2} + Ac_2 + Ac_2^2/K_{i2}} \tag{11}$$

In Eqs. (10) and (11) μ_{2max} and K_{s2} are kinetic coefficients, and K_{i2} is the inhibition constant, (g/L).

Static characteristics

Static characteristics of the BR$_1$

Nullifying the right hand parts of Eqs. (1)-(3) and after some transformations, the following algebraic equations (static characteristics) were obtained:

$$S_1 = -\frac{P_1 + D_1 K_{i1} - K_{i1}\mu_{1max}}{2D_1} \tag{12}$$

$$X_1 = \frac{Y_1 P_1 + D_1 K_{i1} - K_{i1}\mu_{1max} + 2D_1 S_1^{in}}{2D_1} \tag{13}$$

$$Ac_1 = \frac{Y_1 P_1 + D_1 K_{i1} - K_{i1}\mu_{1max} + 2D_1 S_1^{in}}{2D_1 Y_2} \tag{14}$$

$$Q_{H_2} = \frac{Y_1 Y_{H_2} P_1 + D_1 K_{i1} - K_{i1}\mu_{1max} + 2D_1 S_1^{in}}{2} \tag{15}$$

$$P_1 = \sqrt{K_{i1}(D_1^2 K_{i1} - 4D_1^2 K_{s1} + K_{i1}\mu_{1max}^2 - 2D_1 K_{i1}\mu_{1max})} \tag{16}$$

From Eq. (12) the boundary value (after that value wash-out of microorganisms occurs) of the dilution rate (D_{1sup}) was obtained:

$$D_{1sup} = \frac{K_{i1}\mu_{1max} S_1^{in}}{S_1^{in2} + K_{i1} S_1^{in} + K_{i1} K_{s1}} \tag{17}$$

As a result, the admissible region for D_1 is:

$$D_1 \in \left(0, D_{1sup}\right) \tag{18}$$

From the study of static characteristics in Eqs. (13)-(16) and the admissible area of D_1 in Eq. (18), the following conclusions were made:

$$D_{1max} = -\frac{K_{i1}\left(\mu_{1max} S_1^{in2} + K_{i1} K_{s1}\mu_{1max} + K_{i1}\mu_{1max} S_1^{in} \pm P_2 \pm P_3\right)}{P_4} \tag{19}$$

$$P_2 = \mu_{1max} S_1^{in} \sqrt{\frac{K_{s1}(S_1^{in2} + K_{i1} S_1^{in} + K_{i1} K_{s1})}{K_{i1}}} \tag{20}$$

$$P_3 = K_{i1} \mu_{1max} \sqrt{\frac{K_{s1}(S_1^{in2} + K_{i1} S_1^{in} + K_{i1} K_{s1})}{K_{i1}}} \tag{21}$$

$$P_4 = -K_{i1}^2 K_{s1} - K_{i1}^2 S_1^{in} + 4K_{i1} K_{s1}^2 + 4K_{i1} K_{s1} S_1^{in} - K_{i1} S_1^{in2} - 4K_{s1} S_1^{in2} \tag{22}$$

From Eq. (15) and Eqs. (19)-(22) an expression for the maximal value of the hydrogen flow rate (Q_{H_2max}) was obtained:

$$Q_{H_2max} = \frac{P_5}{2(K_{i1} - 4K_{s1})P_7}, \tag{23}$$

$$\begin{aligned} P_5 = {} & 2K_{i1}\mu_{1max} S_1^{in3} Y_1 Y_{H_2} + 4K_{i1}^2 K_{s1}^2 \mu_{1max} Y_1 Y_{H_2} + 2K_{i1}^2 \mu_{1max} S_1^{in2} Y_1 Y_{H_2} - K_{i1}^3 \mu_{1max} Y_1 Y_{H_2} P_7 \\ & -4K_{i1} K_{s1}^2 Y_1 Y_{H_2} P_6 + K_{i1}^2 K_{s1} Y_1 Y_{H_2} P_6 + K_{s1} S_1^{in2} Y_1 Y_{H_2} P_6 + K_{i1}^2 S_1^{in} Y_1 Y_{H_2} P_6 - 4K_{s1} S_1^{in2} Y_1 Y_{H_2} P_6 \\ & -4K_{i1}\mu_{1max} S_1^{in2} Y_1 Y_{H_2} P_7 - 4K_{i1}^2 \mu_{1max} S_1^{in} Y_1 Y_{H_2} P_7 + 4K_{i1} K_{s1} \mu_{1max} S_1^{in2} Y_1 Y_{H_2} \\ & +6K_{i1}^2 K_{s1} \mu_{1max} S_1^{in} Y_1 Y_{H_2} - 4K_{i1} K_{s1} S_1^{in} Y_1 Y_{H_2} P_6 \end{aligned} \tag{24}$$

$$P_6 = \sqrt{\frac{K_{i1}^3 K_{s1} \mu_{1max}^2}{P_8}} \tag{25}$$

$$P_7 = \sqrt{\frac{K_{s1} P_8}{K_{i1}}} \tag{26}$$

$$P_8 = S_1^{in2} + K_{i1} S_1^{in} + K_{i1} K_{s1} \tag{27}$$

Static characteristics of the BR_2

In the same way static characteristics of the BR_2 were obtained:

$$X_2 = \frac{Y_3(Ac_1 D_2 - Ac_1 \mu_{2max} + D_2 K_{s2})}{D_2 - \mu_{2max}} \tag{28}$$

$$Ac_2 = -\frac{D_2 K_{s2}}{D_2 - \mu_{2max}} \tag{29}$$

$$Q_{CH_4} = \frac{D_2 Y_3 Y_{CH_4}(Ac_1 D_2 - Ac_1 \mu_{2max} + D_2 K_{s2})}{D_2 - \mu_{2max}} \tag{30}$$

$$D_{2sup} = \frac{Ac_1 \mu_{2max}}{Ac_1 + K_{s2}} \tag{31}$$

$$D_{2max} = \frac{\pm\mu_{2max}\sqrt{K_{s2}(Ac_1 + K_{s2})} + Ac_1 \mu_{2max} + K_{s2}\mu_{2max}}{Ac_1 + K_{s2}} \tag{32}$$

$$D_{2max} < D_{2sup} \tag{33}$$

After simple transformations for the maximal value of the flow-rate of methane produced in BR_2, the following expression was obtained:

$$Q_{CH_4max} = \mu_{2max} Y_3 Y_{CH_4} \left(Ac_1 + 2K_{s2} - 2\sqrt{K_{s2}(Ac_1 + K_{s2})} \right) \tag{34}$$

Simulation studies

For illustration, the following values of the coefficients of the models in both bioreactors were adopted [10]: Y_1 = 0.08, Y_2 = 1, Y_{H_2} = 1, μ_{1max} = 0.568 h^{-1}, K_{s1} = 3.914, Y_3 = 0.24, Y_{CH_4} = 18.7, μ_{2max} = 0.0083 h^{-1}, K_{s2} = 0.22. For inhibition, the following constants were used: K_{i1} = 1000 and K_{i2} = 10

All variables in the points of maximum and for different values of S_1^{in} are calculated. They are presented numerically in Fig. 2 and Fig. 3.

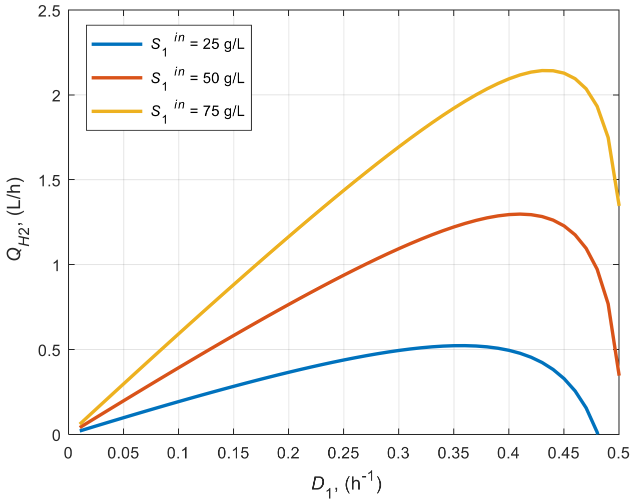

Fig. 2 Two-phases process of anaerobic digestion with production of hydrogen and methane – the flow rate of the hydrogen Q_{H_2}

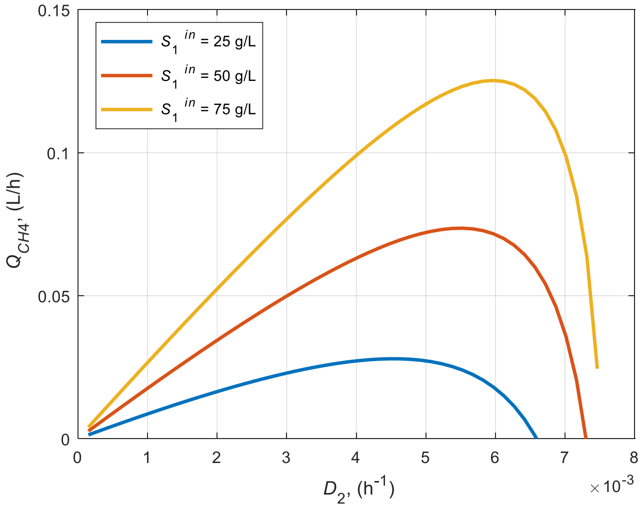

Fig. 3 Two-phases process of anaerobic digestion with production of hydrogen and methane – the flow rate of the methane Q_{CH_4}

It is evident that substrate inhibition imposes its effect on the maximum yield of hydrogen and methane. The obtained results can be also compared to the results of the same process but without substrate inhibition.

Conclusion

A new model of the anaerobic digestion of organic wastes for the simultaneous production of hydrogen and methane in a two-stage process was presented. Substrate inhibition is considered in the model for the two stages of the process. This model is quite simple but presents a case of a significant problem for practice – the substrate inhibition for hydrogen and methane production. New static characteristics have been driven for the case of substrate inhibition, concerning both bioreactors.

The obtained input-output static characteristics for the energy carriers (H_2 and CH_4) could be used to control and optimization of the subjected process.

Further studies could include a depiction of a real process by experimental studies (in laboratory and pilot scale bioreactors) of AD for biotechnological production of hydrogen and methane in two-phase processes from different agricultural wastes. Theoretical comparison with processes without inhibition will lead to more detailed information about the processes of anaerobic digestion for energy production by obtaining an optimized technology (maximal energy production) via the above-presented approach.

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