MODELING OF HYDROGEN PRODUCTION IN BIOFILM REACTORS: APPLICATION OF THE ANAEROBIC DIGESTION MODEL 1

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ABSTRACT

Hydrogen can be produced substantially at a high rate by anaerobic fermentation from organic waste or wastewater. The aim of the work is to model the hydrogen production in anaerobic biofilm reactors using a modeling methodology previously published. The global model combines the dynamics of the three phases present in the reactor including biochemical, physico-chemical and hydrodynamic processes. The Anaerobic Digestion Model No. 1 (ADM1) was selected to calculate the global yield of hydrogen produced from a sugar-based substrate source. As model application, an example based on the start-up and operational performance of an anaerobic fluidized bed (AFB) reactor is presented. Several details of reactor design, biofilm and substrate characteristics, and operational conditions are required for model adjustment and validation. Only the parameter related to biomass transport phenomena was estimated by simulation, and no other parameters had to be modified. Values around $1 \times 10^{-22} \text{dm}^2 \text{g}^{-1}$ were calculated. A good agreement between experimental and predicted values of soluble metabolic products and hydrogen production rate are obtained.

Keywords: Anaerobic biofilm reactors, Bio-hydrogen, Dynamic modeling and simulation

1. INTRODUCTION

Hydrogen gas is an alternative energy source to fossil fuels for energy production. The sustainable generation of hydrogen may be achieved by a range of technologies including biological processes. These include photolysis carried out by algae and cyanobacteria and anaerobic fermentation from organic waste or wastewater [1,2]. However, the hydrogen production rate from fermentation is greater compared to photolysis [3]. The last can not be operated in the absence of light, while fermentative hydrogen production can produce hydrogen all day long without light using various kinds of substrates and has higher hydrogen production stability, simpler control requirements, lower operating costs and higher feasibility for industrialization [4].

1.1 Pathways and pretreatment methods

Although the butyrate-type fermentation is the most popular pathway for fermentative hydrogen production, the ethanol-type fermentation has showed several advantages related to suitable environmental factors such as pH and oxidation-reduction potential [5,6]. In both cases, methanogenesis has to be inhibited. Another pathway that consumes hydrogen is homoacetogenesis. In this process, microorganisms use hydrogen to reduce carbon dioxide to produce acetate. Homoacetogenesis has been usually observed under psychrophilic (15°C) conditions as homoacetogens easily adapt to low temperatures [7], and there are few reports of the existence of homoacetogenesis in continuous systems under mesophilic (37°C), thermophilic (55°C) and hyper-thermophilic (70°C) conditions [2]. The hyper-thermophilic conditions improve the thermodynamic behavior, make the systems less prone to be contaminated with methanogenic microorganisms and increase the pathogenic destruction of residues [8]. In order to enrich hydrogen producing microorganisms and to establish high-efficient communities of the mixed microbial cultures, inoculum needs to be pretreated before the cultivation. Ren et al [9] investigated some pretreatment methods on the seed sludge from a municipal wastewater treatment plant, including heat-shock, acid, alkaline and repeated-aeration methods. As results, the heat-shock, acid and repeated-aeration pretreatment methods completely suppressed the methanogenic activity of the seed sludge, but the alkaline pretreatment...
did not. The pretreatment methods substantially affected the species composition of microbial communities and it resulted in the change in fermentation types. Butyric acid type fermentation was achieved by the heat-shock and alkaline pretreatments, mixed-acid type fermentation was achieved by acid pretreatment, and ethanol-type fermentation was observed by repeated-aeration pretreatment. The highest hydrogen yield of 1.96 mol per mol of glucose was observed with the repeated-aeration pretreatment method, while the lowest was obtained as the seed sludge was acidified.

1.2 Kinetics and reactors

Recently, Wang and Wan [4] published a review on kinetic models for fermentative hydrogen production. These models have been used to describe the progress of a batch fermentative process, to investigate the effects of substrate concentration, inhibitor concentration, temperatures, pH, and dilution rates, and to establish the relationship among the substrate degradation rate, the growth rate of hydrogen-producing microorganisms and the product formation rate. In example, the modified Gompertz model has been widely used to describe the progress of a batch fermentative hydrogen production process, while Monod model has been widely used to describe the effects of substrate concentration. The Andrew model has been used to describe the effects of H+ concentration on the specific hydrogen production rate, while the Luedeking-Piret model and its modified form have been widely used to describe the relationship between the microorganism growth rate and the product formation rate.

The Anaerobic Digestion Model No. 1 (ADM1) framework offers a remarkable flexibility for describing the performance of both pure and mixed cultures in either batch or continues systems [10]. Recently, an ADM1-based kinetic model was used to simulate the hydrogen production process in batch and continuous cultures of the bacterium Ruminococcus albus grown on sweet sorghum extract as the sole carbon source [11]. Sorghum extract contains soluble sugars such as sucrose and glucose. Since sucrose is a dimer composed of the monomers glucose and fructose, i.e. two hexoses with the same molecular structure, the generation of metabolites during its fermentation was expected to follow the same pattern with that of glucose fermentation. The authors showed that the modified ADM1 model was successful in adequately describing the behavior of the microorganism on the real sugar-based substrate. However, this modified kinetic model only includes formate, acetate, ethanol and hydrogen as fermentation products, and thus, the presence of other metabolites such as propionate, butyrate and valerate can not be investigated.

With respect to the continuous mode operation in hydrogen production, various types of reactors were employed [12], among which continuously stirred tank reactor (CSTR) was mostly reported. Although stirring operation could improve mass transfer efficiency, the suspended-cell systems suffer the biomass washout problem at high organic loading rate (OLR). On the other hand, the immobilized-cell systems allow to maintain higher biomass concentration even at high ORLs. There are some “high rate” anaerobic reactors that have been used for the bio-hydrogen production, such as anaerobic fluidized beds (AFB) [12,13,14], upflow anaerobic sludge blanket (UASB) reactors [15,16], and expanded granular sludge blanket (EGSB) reactors [2,17]. However, few operational strategies have been proposed for a continuous-flow reactor with regard to high effective hydrogen production.

In previous works, heterogeneous models for three-phase AFB, UASB and EGSB reactors for wastewater treatment were developed and validated [18,19,20,21,22]. These modeling approaches combine the dynamics of the three phases present in the reactor including biochemical, physico-chemical and hydrodynamic processes. The aim of this work is to apply this methodology for modeling the hydrogen production in biofilm reactors. Although the substrate degradation scheme described in the original ADM1 does not identify the ethanol as a metabolite, this model has been selected here to calculate the global yield of hydrogen produced from a sugar-based substrate source. Figure 1 represents the degradation steps and microorganism trophic groups assumed in ADM1.

Due to space restrictions, only one example is presented; an AFB application is selected. It is based on the experimental results obtained by Guo et al. [12] operating a bioreactor with a working capacity of 3.35 L, fed with molasses and using a mixed microbial culture and granular activated carbon (GAC) as biofilm support media. Other application examples, based in different reactor configurations, could be presented in an extended version of the paper.
(3) the hydrodynamics model, describing characteristics of phase mixture and flow patterns.

The authors invite readers to consult the papers quoted in the text, where the main hypotheses are discussed and model mathematical equations are presented.

3. COMPUTATIONAL ASPECTS

The mathematical model was implemented and solved using the process modeling software tool gPROMS (Process Systems Enterprise Ltd.). A “high-index” DAE system (index > 1) was verified [23].

Low steady state concentration values are considered as initial values for the biological and chemical species. The total CPU time required to solve the case study, described in the following section, is about 11 s on an 800MHz Pentium IV PC.

4. RESULTS AND DISCUSSION

4.1 Case study

An existing set of experimental data obtained by Guo et al. [12] based on the startup and operational performance of an AFB reactor, is used here to show model application. Details of reactor design, sludge and substrate characteristics, and operational conditions are summarized in Table I. Although in the original paper this system was classified as an EGSB reactor, the authors prefer to analyze the system as an AFB configuration since a support media (GAC) was used for biofilm attachment. Molasses, obtained from a local beet sugar refinery and basically composed by sucrose as a chemical oxygen demand (COD) source, was used as reactor feeding. One liter of an inoculating sludge with 8.49 g dm⁻³ of volatile suspended solids (VSS), and pretreated with an aeration method, was seeded into de AFB system before startup. No pH regulation was performed during the whole operation and the temperature was keeping at 35±1 °C. The organic loading rate was increased step by step, by increasing the COD or shortening hydraulic retention time (HRT) as shown in Table I. The recycle flow provided upflow velocities for media in order to maintain a bioparticles expansion level of 8-10%.
Parameter (dimension) | Value
---|---
Reactor design |  
Working reactor volume (dm³) | 3.35  
Inner diameter (dm) | 0.60  
Height of the water level (dm) | 12.00  
Bioparticle characteristics |  
Inoculating sludge conc. (g dm⁻³) | 8.49  
Biomass density (g dm⁻³) | 1026  
Support initial load (gGAC) | 330.6  
Support mean diameter (10² dm) | 1.5-2.0  
Support density (g dm⁻³) | 1420  
Wastewater characteristics |  
Influent pH | nd  
Substrate composition | Sucrose (Molasses)  
Hydrodynamic characteristics |  
Static bed height (dm) | 4.0  
Bed porosity (dm³ dm⁻³) | 0.77  
Influent flow rate (dm³ d⁻¹) | 13-80  
Liquid upflow velocity (10⁻³ dm d⁻¹) | 54-61 (See Fig. 5)  
Operational characteristics |  
Biomass concentration (g dm⁻³) | 17.1 (average)  
Temperature (°C) | 35±1  
Step (Time) (d) | OLR (gCOD dm⁻³ d⁻¹) | HRT (d) | COD (mg dm⁻³) | pH average
I (1-6) | 8 | 6 | 2000 | 5.33
II (7-13) | 12 | 4 | 2000 | 4.36
III (14-20) | 24 | 4 | 4000 | 4.66
IV (21-27) | 36 | 4 | 6000 | 4.33
V (28-35) | 48 | 4 | 8000 | 4.12
VI (36-42) | 96 | 2 | 8000 | 4.48
VII (43-51) | 192 | 1 | 8000 | 3.88
VIII (52-59) | 96 | 2 | 8000 | 4.21
IX (60-150) | 120 | 2 | 10000 | 4.36

Table I. Details of AFB reactor used as model application [12].

4.2 Reactor performance and model results

Simulation results for (influent and effluent) OLR, pH, hydrogen production rate (HPR) and specific hydrogen yield (HY) are depicted in Figure 2. HPR and HY experimental values, scanned from a bitmap format of the original graph, have been also included. In general, a good agreement between experimental and predicted values of HPR was obtained. A maximum HPR value of 0.71 dm³ dm⁻³ h⁻¹ was achieved at pH 4.2–4.4. At the same time, the hydrogen yield (HY) peaked at 3.47 mol per mol of converted sucrose. Simulation results do not agree with HY experimental values at initial steps of the startup policy. In our experience, measurements of gas flow rate using a water replacement method in AFB reactors can result unsatisfactory at initial stages of reactor startup. Model responses for the gaseous products, such as gas flow rate (Qg_out) and gas partial pressure (p_gas), are shown in Figure 3. As reported, the biogas is composed of hydrogen (H₂) and carbon dioxide (CO₂), and free of methane (CH₄). The operational pH level assures these results.

![Figure 2. Simulation results for influent and effluent OLR and pH. Experimental and predicted values for hydrogen production rate (HPR) and specific hydrogen yield (HY).](image)

![Figure 3. Simulation results for biogas flow rate (Qg_out) and gas partial pressure (p_gas) of hydrogen (H₂), carbon dioxide (CO₂) and methane (CH₄).](image)

![Figure 4. Simulation results for soluble metabolic products: acetate (S_{HAc}), propionate (S_{Prp}), butyrate (S_{HBut}) and glucose (S_{Go}). Experimental and predicted values for HPR.](image)
This behavior is modeled in ADM1 by using an empirical (low) pH inhibition function assumed for acidogens, acetogens and methanogens; and a non-competitive \( H_2 \) inhibition function assumed for acetogens [10]. The predicted hydrogen volume is around 60\% of total biogas (values up to 53\% were reported). Besides \( H_2 \), \( CO_2 \) and \( CH_4 \), water vapor is considered in the gas phase, and an Antoine-type equation is used to calculate its partial pressure. Figure 4 shows predicted values of soluble metabolic products, such as glucose and volatile fatty acids (only acetate, propionate and butyrate are shown). Here, experimental values have not been included since the original data resulted illegible for the scanning method. No experimental data for glucose were found. Simulation results agree for butyrate and valerate concentrations. Propionate concentration values resulted higher than the experimental ones. As mentioned, ethanol is not identified as a metabolite in ADM1 and this component seem to be quoted in the acetate concentration values. An adequate modification should be implemented in the kinetics model to obtain accurate results. Low COD removal levels are reached during anaerobic fermentation for obtaining hydrogen (see Fig. 2). Therefore, a COD reduction method should be applied to treat the process effluent.

4.3 Sensitivity analysis

Several details of reactor design, biofilm and substrate characteristics, and operational conditions are required for model adjustment and validation. Almost all works published describe better the biochemical performance of reactors than their hydrodynamics. Due to the lack of information on some parameters that can be measured and are not reported, the authors should solve the initialization problem via simulation, i.e. a sensitivity analysis of model results related to these parameters is required. In this work, only a parameter related to biomass transport phenomena, the specific biofilm detachment rate \( (k_E) \), was estimated by simulation. No other (biological, hydrodynamic, physico-chemical) parameters had to be modified.

Figure 5 shows the sensitivity analysis of HPR in relation to \( k_E \). An initial value of \( 1 \times 10^{-22} \text{ dm}^2 \text{ g}^{-1} \) was used. As observed, an increase in the \( k_E \) value causes a decrease in the hydrogen production rate. In practice, the suspended biomass concentration in the effluent stream increases and some microorganisms leave the bioreactor. Model responses for attached biomass concentration and hydrodynamic characteristics, such as reactor height (H) and bioparticle mean diameter \( (d_{bp}) \), have been also included in Figure 5. It was observed that the solid holdup decreases when parameter \( k_E \) increases, and hydrodynamic conditions vary in AFB reactors [18,19]. Bioparticles with less mean diameter, and higher density, are assumed to be fluidized in lower extension causing a decrease in the height of reactor (see Fig. 5). Upflow velocity \( (U_o) \) values were calculated in order to maintain the bioparticles expansion level of 8-10\%, as reported. The risk of working with small and low-density bioparticles, such as the GAC-type, is the biomass washout when high upflow velocities are applied for bed expansion. In the original source, authors estimated an average value of 17.1 g dm\(^{-3}\) for attached biomass concentration. As observed in Figure 5, a value of 14 g dm\(^{-3}\) is predicted at OLR of 120 gCOD dm\(^{-3}\) d\(^{-1}\), assuming a \( k_E \) value of \( 1 \times 10^{-22} \text{ dm}^2 \text{ g}^{-1} \).
4.4. EGSB model applications

EGSB reactor model results analogous to AFB model. The main differences between both technologies are based on characteristics of the solid phase (bioparticles) and hydrodynamics. A discussion on these aspects, including the main mathematical equations, has been recently published [22]. Similar to $k_b$ in AFB reactor, a novel parameter was defined to explain how the process of granulation is affected by environmental and operational conditions; and has to be also estimated for model adjustment. A good agreement was obtained for an EGSB application, including a comparison with an AFB configuration and using the experimental data published by Zhang et al. [17]. Results could be presented in an extended version of the paper.

5. CONCLUSIONS

For the example analyzed here, the ADM1-based AFB reactor model, adjusted by calculating the parameter related to biomass transport phenomena, was able to reproduce the main successes of the bioreactor for hydrogen production. Simulations agree satisfactorily with the main experimental observations, without modifying any other parameter. The model is able to resist strong numerical disturbances to represent a “step by step” start up of the reactor and computes the interaction between hydrodynamic events and biological performance of bioreactor.

The model allows predicting profiles of non-macroscopic variables such as substrates and biological species concentration. However, kinetics model should be modified to obtain more precise information on the investigated system; i.e. ethanol has to be included as metabolite in the model for hydrogen production applications.

6. REFERENCES