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Research paper

Process simulation and modeling: Anaerobic digestion of complex organic matter

S. Mani, J. Sundaram*, K.C. Das

College of Engineering, University of Georgia, 597 Drew Brooks Drive, Athens, GA 30602, United States

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ABSTRACT

This work is focused on evaluating kinetic models of complex organic matters hydrolysis and volatile fatty acids degradation in anaerobic digestion process, simulated using SuperPro design software. Kinetic model evaluation was also carried for simulated integrated system of liquid anaerobic digestion (LAD) of dairy manure and solid state anaerobic digestion (SS-AD) of corn stover. Already developed hydrolysis and volatile fatty acid (VFA) degradation kinetic constants were used to simulate anaerobic digestion processes of dairy manure and corn stover separately and in the integrated process as well. Hydrolysis of complex soluble organic matters such as protein, carbohydrate and fat was modelled using first-order kinetics. Monod model was tested for the VFAs such as acetic, propionic and butyric acid degradation and biogas production. Comparative study has been done between the experimental data published already and results obtained from SuperPro simulated processes. The simulated results were well comparable with the experimental results.

1. Introduction

Anaerobic digestion of complex organic matter is described as sequential process steps involving hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is often rate limiting when the particulate matter is not readily degradable or in systems with high loading rates. Even though the dynamics of hydrolysis of some individual substrates are known, the process is often described as a simple first-order process due to extensive variations in substrate composition [1,2]. The cumulative effects of various processes during hydrolysis were simplified to single first-order kinetics for the substrate biodegradation. However, sometimes relatively high hydrolysis rates were reached in anaerobic biodegradability tests particularly when there is a high inoculum-to substrate ratio. It shows that degree of hydrolysis depends on biomass concentration or their activity. Some of the previously published work says that the first order kinetics of hydrolysis is not applicable in all circumstances. The objective of this paper is to test the first order kinetics for hydrolysis of dairy manure and corn stover constituents to compare their sensitivity to the simulated liquid anaerobic digestion (LAD) and solid state anaerobic digestion (SS-AD) process and the goodness of this model was compared with the available experimental data in the published literatures. A wide range of hydrolysis rate constants of carbohydrates, proteins and fats have been reported assuming first-order hydrolysis. However, it should be taken into account that the substrate hydrolysis rate depends very much on the origin and the previous acclimation of the anaerobic culture.

During anaerobic digestion of organic matter monosaccharides, amino acids and long chain fatty acids, hydrolysis products, volatile fatty acids (acetate, butyrate, propionate, lactate, etc.) and hydrogen are formed. They all are the precursors for methane production. When a process is composed with sequences of reactions, the overall rate is determined by the slowest reaction, named the rate-limiting step [3]. Hydrolysis is the rate-limiting step in anaerobic digestion generally [1]. Acidogenesis after hydrolysis is the quickest step during the anaerobic digestion of complex organic material. For efficient methane production it is important to have a balance between the reactions rates of the different steps involved in the anaerobic digestion. Acetate is the main precursor of more than 75% of methane production during anaerobic digestion [4]. Propionate and Butyrate are other

* Corresponding author.
E-mail address: jayas@engr.uga.edu (J. Sundaram).

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important VFA which are further converted into acetate and hydrogen. Most of the research papers on anaerobic digestion modeling concluded that except hydrolysis other sub process could be modeled successfully using Monod kinetics. Some said that the Haldane kinetic coefficients were much more constant than Monod kinetic coefficients [5]. In this present work Monod kinetic model was tested for VFA degradation and compared with the available experimental data in the published literatures. Kinetic constants of VFA degradation models were collected from the previously published articles [6]. When the anaerobic digestion process is successfully proceeding, the concentration of VFA would be less than 250 mg/L. In order to achieve better digestion process, high acid concentrations that associated with digestion process failure should be avoided. Therefore, continuous degradation of VFA is an essential process to enhance biogas production.

2. Method

2.1. Model development

The process models were developed using SuperPro designer (Intelligent, Inc., Scotch Plains, NJ) for an anaerobic digestion plant that integrates dairy manure and corn stover for biogas production. The liquid anaerobic digester capacity was designed to handle 250 ton/day of dairy manure with 5% solid content at the temperature of 37 °C. Biogas production by integrating liquid and solid state anaerobic digestion process was divided into different sections such as receiving liquid dairy waste manure, dilution, fiber removal, anaerobic digestion, gas production and effluent storage. Integrated LAD and SS-AD process was designed for corn stover hydrolysis, blending of hydrolyzed corn stover with LAD effluent, feeding this entire mix for digestion, biogas production through anaerobic digestion and collection of digestate for manure purpose. Biogas produced by LAD and SS-AD can be mixed in the process design and then cleaned for separating bio-methane from carbon dioxide, ammonia and hydrogen sulfide mix through gas absorption process using water. Process design for LAD and SS-AD systems were simulated individually and compared with the methane production rate of the integrated system. Kinetic models for hydrolysis and VFA degradation inside the digester were evaluated individually for LAD and SS-AD with LAD effluent.

2.2. Process design elements of LAD (dairy manure) system

Manure collection and handling is the key considerations to design an AD system which includes the amount of water and total solids of the manure. Additional solids are added from wasted feed, free stall bedding, and soil tracked in from outside lots. Additional water is added from water wastage, milking center waste water, water used to clean floors, and flushing of alleys. After manure collection, manure pretreatment such as screening, grit removal, mixing, were designed to adjust the manure water and total solid contents. To avoid the mixing of sand and rocks into the digester a concrete or metal mixing tank was used to settle some of the major solids like rocks. Then it was sent through solid separator/screening to remove other solids such as bedding fiber materials. Belt filtration separator was used in the SuperPro simulation model to recover coarse solids and fibers.

Anaerobic digestion: Anaerobic digestion of complex organic dairy manure involves, hydrolysis, liquefaction, and fermentation; (2) hydrogen and acetic acid formation; (3) methane formation.

At the beginning hydrolysis did take place to reduce complex organic biomass into simple soluble molecules by extracellular enzymes. Proteins, lipids and carbohydrate polymers were hydrolyzed to amino acids, long-chain fatty acids, and sugars, respectively. The reduced compounds were then converted by fermentative bacteria to a mixture of short chain volatile fatty acids (VFAs) and other products such as carbon dioxide, hydrogen and acetic acid. Acetogenic bacteria further converted the organic acids to acetate, carbon dioxide, and/or hydrogen which were the direct substrates for methane production. The final step was methanogenesis, where a variety of methanogenic bacteria consumed acetate, carbon dioxide, and hydrogen to produce methane. Methanogenesis is the focus of many AD studies due to its sensitivity to feedback inhibition by acidic intermediates. The heterogeneous nature of the substrate in SS-AD systems creates more ideal micro-environments for the growth of each microbial family that are required to complete the digestion process. So the culture in fermentation processes behaves quite differently in solid substrates [7].

2.2.1. Hydrolysis, liquefaction, and fermentation

Hydrolysis and liquefaction step convert the complex organic materials into nutrient source that can pass through the bacteria cell wall to serve energy for their survival; i.e., Protein, carbohydrate, cellulose, and hemicellulose in the manure are hydrolyzed and metabolized into mainly short-chain fatty acids—acetic, propionic, and butyric—along with CO_2 and hydrogen (H_2) gases. At this stage the decomposition products have noticeable, disagreeable, effusive odors from the organic acids, H_2S, and other metabolic products. Hydrolysis and liquefaction are accomplished by extracellular, hydrolytic enzymes produced and excreted by the bacterial population. Proper functioning of hydrolysis step is more important for the stabilization of complex organic manure. Rate hydrolysis limits the overall rate of stabilization and fermentation. During hydrolysis, there should be sufficient quantity of extracellular hydrolytic enzymes produced by the bacteria, so that it can have intimate contact with complex organics without limiting the overall stabilization reaction. So it is important to maintain the uniform mixing and temperature and concentrated organic substrate and the microbial population inside the digester system. Volatile solids reduction in anaerobic digestion is different in different plants, which depends on the manure characteristics and its upstream processing. Glucose is the most common substrate in anaerobic digestion and it is obtained from hydrolysis of macromolecules such as carbohydrate (polysaccharides). Glucose degradation in anaerobic digestion includes multiple biochemical reactions as given below along with microbial degradation [8].

$$C_6H_{12}O_6 \rightarrow CH_3COCOOH + CH_3COOH + HCOOH + C_2H_5OH$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_3COOH + 2H_2O$$

$$C_6H_{12}O_6 \rightarrow CH_3(CH_2)_2COOH + 2H_2 + 2CO_2$$

After the hydrolysis of complex organics, fermentation takes place on long chain organic acids, sugars, amino acids to convert them in to smaller organic acids such as propionic-, butyric and valeric acid, which is called acid forming phase or fermentation phase. Acetic acid, hydrogen, and carbon dioxide are also formed during the production of organic acids in acid forming phase. Hydrogen is inhibitory to many of the acid-forming bacteria and must be removed from the system if acid production is to continue. However, hydrogen is an energy source for some methanogenic bacteria and is rapidly consumed in the reduction of carbon dioxide to methane.