Energy 102 (2016) 1–9

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Kinetics of methane production and hydrolysis in anaerobic digestion of corn stover

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ARTICLE INFO

Article history:
Received 23 December 2015
Received in revised form
8 February 2016
Accepted 12 February 2016
Available online xxx

Keywords:
Anaerobic processes
Biogas
Modelling
Kinetic parameters
Hydrolysis
Nonbiodegradable

ABSTRACT

In order to develop a time-saving method for determination of ultimate methane production, obtain the hydrolysis kinetic constant, and identify a determination method for the nonbiodegradable organic fraction of substrate (VS_{NB}) of green and air-dried corn stover, the kinetics of methane production and hydrolysis were studied using batch tests. The results showed that the conventional first-order hydrolysis kinetic model was not suitable for describing the entire hydrolysis process of corn stover, because there were two first-order decay periods for hydrolysis of corn stover. The hydrolysis kinetic constants $k_{H,1}$ and $k_{H,2}$ of the first and second periods were 0.1701 and 0.0415 1/d for green stover and 0.1052 and 0.0360 1/d for air-dried stover. The value of VS_{NB} could be obtained by the graphical method rather than by the hydrolysis kinetic model. The obtained VS_{NB} contents were 12.9% and 24.7% of VS (volatile solid) for green and air-dried stover, respectively. The ultimate methane production and corresponding digestion time could be understood through the methane production kinetic model by digestion experiments within a short time. The ultimate methane productions were 347.1 and 319.4 mL/g based on VS and the corresponding digestion times were 69.2 and 182.3 days for green and air-dried stover, respectively.

1. Introduction

The Methane yield potential and methane production rate of substrates are two important indices for anaerobic biogas production. Correspondingly, the biodegradable organic fractions and hydrolysis rates of substrates are two important parameters for anaerobic biodegradation. In fact, these parameters determine, to a certain extent, both the design and economic details of biogas plants.

Anaerobic batch tests are the standard method for the determination of methane yield potential of substrates [1]. When performing a batch test, the decision of when to terminate the experiment is crucial. In 2006, the Association of German Engineers (VDI) published the guideline VDI 4630, "Fermentation of organic materials, characterization of the substrate, sampling, collection of material data, fermentation tests" [2]. This guideline introduces the so-called 1% criterion, in which the experiment is continued until the daily gas production is less than 1% of the total gas production. Many experiments have been performed according to this guideline [3–6].

The ultimate methane production, known as the BMP (biochemical methane potential) of the substrate, is theoretically reached after infinite incubation. In 2009, a guideline for BMP assays was proposed by the 'Task Group for the Anaerobic Biodegradation, Activity and Inhibition of the Anaerobic Digestion' of the IWA (International Water Association) [7]. In this protocol, batch experiments were not considered complete until no methane was produced. This protocol is now the BMP test basis for most of experiments performed. The methane potential of wheat straw stillage was determined in 118 mL serum bottles with working volume of 40 mL [8]. The small and large BMP assays of grass silage were carried out in small serum bottles and 1.5 L reactor, respectively [9]. BMP test was conducted in 240 mL serum bottle with working volume 100 mL using beef feedlot manure as substrate [10]. BMP tests were carried out at different scales (5 L and 0.5 L) for both wet

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http://dx.doi.org/10.1016/j.energy.2016.02.074
0360-5442/

and dried food waste [11]. However, BMP assays require long experimental times, and the method proposed by VDI 4630 does not yield the true ultimate methane production.

Anaerobic degradation of particulate organic matter involves a complex network of reactions in series and in parallel involving several key groups of bacteria. Hydrolysis of particulate matter to soluble substrates is often assumed to be the rate-limiting step in anaerobic digestion. Substrate hydrolysis and biogas production typically follow first-order kinetics when macro- and micro-nutrients are available and there is no inhibition [12–14]. To date, first-order kinetics have been used to model the hydrolysis process of anaerobic digestion of organic fractions of municipal solid waste [14], sunflower oil cake [15], and mixtures of manure, animal feed, slaughterhouse waste, and municipal solid waste [13] in batch mode. However, there are no first-order hydrolysis kinetics studies of corn stover. Moreover, the values of the hydrolysis kinetic constants (k_H) of these models were calculated indirectly from data of methane production rather than substrate reduction. Notably, the nonbiodegradable organic fraction of the substrate cannot be obtained by using traditional first-order hydrolysis kinetics.

The aims of this study were to develop a time-saving method for determination of ultimate methane production and corresponding digestion time, to identify an appropriate determination method for the nonbiodegradable organic fraction of substrate, and to obtain the hydrolysis kinetic constant of corn stover.

2. Material and methods

2.1. Substrates and inoculums

Green and air-dried corn stover with harvest time of 6 and 8 months, respectively, were obtained from rural Chengdu, China. The collected stover was chopped and sieved to particles measuring less than 5 mm in size. The sieved green corn stover was stored at 4 °C. The residue left on a 1-mm sieve of material taken from a mesophilic (37 °C) anaerobic digester fed with pig manure was used as the inoculum. The anaerobic digestion of the inoculum was conducted untill no biogas production in order to ignore the methane production of the inoculum itself. The characteristics of the substrates and inoculum are listed in Table 1. The lignin and cellulose contents of air-dried corn stover were higher than that of green corn stover, since the serious lignification was occurred for air-dried corn stover.

2.2. Experimental setup and operation

A 250-mL bottle with working volume 200 mL was used for the batch anaerobic digestion tests. The bottle was sealed using a rubber stopper with a pipe for extracting the biogas. The reactor was connected to a gas collection system consisting of a saturated brine displacement bottle and a brine gathering bottle. The initial substrate concentration was about 30 g/L based on TS (total solid). The batch reactors were filled with 30 g of green corn stover or 6.5 g of air-dried corn stover before adding inoculum to a total weight of 200 g. The VS (volatile solid) ratio of substrate to inoculum was 1.44 and 1.29 for batch digestions of green and air-dried corn stover. Each test of green and air-dried corn stover had 20 reactors in parallel. Prior to operation, the reactors were flushed with nitrogen for 5 min to ensure anaerobic conditions. The digesters were placed in a water bath at 35 ± 1 °C. Each reactor was manually mixed twice a day. The experiment was carried out for 20 days. Two reactors were randomly removed for measurement of the TS and VS (volatile solid) contents of the digested residues at different times (Table 2).

2.3. Analytical methods

The TS and VS contents were determined using standard techniques [16]. Analyses for C and N were conducted using a Vario EL element analyzer (Elementar Analysensysteme GmbH, Germany). Cellulose, hemicellulose, and lignin contents were determined as previously described [17].

Biogas production was estimated by measuring the water displacement. Biogas analysis was performed using an Agilent 6890 GC (gas chromatography) system (Agilent Technologies, USA) with a TCD (thermal conductivity detector) and a 2-m stainless steel column packed with Porapak Q (50/80 mesh). The operating temperatures at the injection port, column oven, and detector were 200, 80, and 200 °C, respectively. Argon was used as the carrier gas at a flow rate of 30 mL/min.

2.4. Process fitting and first-order kinetic model

2.4.1. Methane production fitting model

A modified Gompertz model (Eq. (1)) was used to fit the data of methane production [18]:

$$M(t) = P \cdot \exp\left\{ -\exp\left[\frac{R_m \cdot e}{P} \cdot (\lambda - t) + 1\right]\right\} \quad (1)$$

where M is the cumulative methane production (L/kg_{VS}) at a fermentation time t (d), P is the maximum cumulative methane production (L/kg_{VS}) for the entire experimental digestion time, R_m is the maximum methane production rate ($L/(kg_{VS} \cdot d)$), and λ is the lag-phase time (d). The values of P, R_m, and λ were obtained by data fitting.

The methane production rate (Eq. (2)) was obtained by differentiating the modified Gompertz equation,

Table 2
Substrate concentrations during the digestion of corn stover.

Time (d)	Green corn stover		Air-dried corn stover	
	TS (g/L)	VS (g/L)	TS (g/L)	VS (g/L)
0	30.3 ± 0.8	26.9 ± 0.6	31.0 ± 0.9	28.6 ± 0.8
1	24.2 ± 0.6	21.2 ± 0.5	30.9 ± 0.8	26.4 ± 0.8
2	20.7 ± 0.6	18.7 ± 0.6	26.3 ± 0.7	23.2 ± 0.7
3	18.9 ± 0.7	16.3 ± 0.5	24.4 ± 0.8	20.9 ± 0.7
5	17.3 ± 0.5	14.9 ± 0.4	22.4 ± 0.6	19.3 ± 0.5
7	16.6 ± 0.4	13.8 ± 0.3	21.5 ± 0.6	18.2 ± 0.6
9	16.0 ± 0.3	13.7 ± 0.4	–	–
10	–	–	19.1 ± 0.5	16.1 ± 0.5
12	14.0 ± 0.5	12.2 ± 0.2	17.9 ± 0.4	14.6 ± 0.4
15	13.1 ± 0.4	9.6 ± 0.3	16.8 ± 0.5	13.6 ± 0.5
18	12.3 ± 0.3	8.7 ± 0.2	15.9 ± 0.4	12.5 ± 0.4
20	11.4 ± 0.3	8.1 ± 0.2	14.1 ± 0.4	11.1 ± 0.3

Table 1
Main characteristics of the substrates and inoculum.

Materials	Total solid (%)	Volatile solid (%)	C/N	Hemicellulose (%VS)	Cellulose (%VS)	Lignin (%VS)
Green corn stover	20.2 ± 0.7	17.9 ± 0.7	28.5 ± 1.1	31.8 ± 0.9	39.8 ± 1.1	11.0 ± 0.3
Air-dried corn stover	91.4 ± 3.8	84.2 ± 2.9	26.0 ± 0.9	24.0 ± 0.8	44.0 ± 1.3	14.1 ± 0.5
Inoculum	3.6 ± 0.1	2.2 ± 0.1	11.8 ± 0.3	–	–	–