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Effect of thermal, acid, alkaline and alkaline-peroxide pretreatments on the biochemical methane potential and kinetics of the anaerobic digestion of wheat straw and sugarcane bagasse

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HIGHLIGHTS

- Highest methane productions were obtained from thermally pretreated whole slurries.
- Furfural and 5-HMF released in acid pretreatment inhibited methane production.
- High phenolic compounds release required a microorganism's acclimation period.
- Lignin degradation provided the highest hydrolysis rates when inhibition was defeated.
- A novel kinetic model is proposed combining hydrolysis and microorganisms inhibition.

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ABSTRACT

The effect of thermal, acid, alkaline and alkaline-peroxide pretreatments on the methane produced by the anaerobic digestion of wheat straw (WS) and sugarcane bagasse (SCB) was studied, using whole slurry and solid fraction. All the pretreatments released formic and acetic acids and phenolic compounds, while 5-hydroxymetilfurfural (HMF) and furfural were generated only by acid pretreatment. A remarkable inhibition was found in most of the whole slurry experiments, except in thermal pretreatment which improved methane production compared to the raw materials (29% for WS and 11% for SCB). The alkaline pretreatment increased biodegradability (around 30%) and methane production rate of the solid fraction of both pretreated substrates. Methane production results were fitted using first order or modified Gompertz equations, or a novel model combining both equations. The model parameters provided information about substrate availability, controlling step and inhibitory effect of compounds generated by each pretreatment.

1. Introduction

Bioenergy production from renewable sources is becoming crucial in order to address the growing demand for energy and the need to reduce greenhouse gas emissions, owing to the unavoidable depletion of fossil fuel reserves and the environmental consequences of global warming (Karagöz et al., 2012).

Among renewable sources, the lignocellulosic biomass is one of the most attractive alternatives for bioenergy production (second generation technology) since it is available in high quantities and at a low cost (Badshah et al., 2012). This study focuses on bioenergy production from two of the major agricultural lignocellulosic residues: wheat straw (WS) and sugarcane bagasse (SCB). Wheat straw represents the largest fraction of agricultural waste in many countries, including Spain. Most of this wheat straw is commonly used for mulching or as fodder and the rest is burnt or left unused. For this reason, its use for biofuel production is growing worldwide (Menon and Rao, 2012). Sugarcane bagasse is an abundant lignocellulosic residue produced in many tropical countries, such as Brazil, India and Colombia. This bagasse is commonly used for generating electricity by combustion, as animal feedstock,

Abbreviations: BMP, biochemical methane potential; NP, normalized production of methane; SCB, sugarcane bagasse; TS, total solids; TKN, total Kjeldahl nitrogen; VS, volatile solids; WS, wheat straw.

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or as fuel in boilers that produce low-pressure steam. However, the surplus that remains leads to environmental and storage problems (Costa et al., 2014; Travaini et al., 2013).

Three types of energy can be produced from these lignocellulosic wastes through thermochemical or biochemical processing: liquid fuels such as bioethanol, gaseous fuels such as biogas, and electricity by combustion (Menon and Rao, 2012).

Biogas, composed mainly of methane and carbon dioxide, is considered a clean and renewable form of energy. It has the advantage of being easy to implement for consumers, and easy to produce on a local level, such as small-scale farms (Taherdanak and Zilouei, 2014). Biogas can be produced through the anaerobic digestion of many types of wastes, and is considered one of the most efficient technologies, since high energy recovery and environmental benefits can be achieved (Ferreira et al., 2013).

Nevertheless, the biodegradability of biomass residues is limited by its lignocellulosic structure. Therefore, efficient pretreatment digestion could accelerate the hydrolysis and improve the biogas production (Sambusiti et al., 2013). However, the realization of a pretreatment frequently produces degradation compounds that can act as inhibitors: organic acids (acetic, formic and levulinic), furan derivatives [furfural and 5-hydroxymethylfurfural (5-HMF)] and phenol compounds, affecting overall cell physiology and often decreasing viability and productivity (Chandel et al., 2011).

Different pretreatment methods have been studied, depending on the characteristics of each lignocellulosic feedstock (Karagöz et al., 2012), including biological, chemical, physical processes, or a combination of them. Among them, this work focuses on thermal, dilute acid, dilute alkaline and oxidative pretreatments.

The thermal pretreatments are considered eco-friendly, green processing technologies. Energy recovery from biomass for fuel is excellent, often with values as high as 80% (Chandra et al., 2012a). Thermal pretreatments have been applied to improve the anaerobic digestibility of different agriculture substrates such as wheat straw, sorghum forage and sugarcane bagasse (Costa et al., 2014; Sambusiti et al., 2013). The non-addition of chemicals avoids the corrosion problems, and decreases the formation of toxic compounds. Other advantages include the lower requirement of chemicals for the neutralization of the hydrolysates produced, and the smaller amount of waste produced in comparison to other processes (Ferreira et al., 2013).

Acid pretreatment is widely applied due to its low cost and high efficiency to hydrolyze hemicellulose into monomeric sugars without dissolving lignin (Ferreira et al., 2013). However, this pretreatment is corrosive and generates high concentrations of toxic compounds, making it necessary to recover the acids in order to make the process economically feasible (Talebnia et al., 2010). The main substrates studied for this pretreatment are wheat straw, sorghum forage and sugarcane bagasse (Sambusiti et al., 2013), and different acids such as sulphuric, hydrochloric, phosphoric, maleic, peracetic or nitric acids have been investigated (Badshah et al., 2012; Chandel et al., 2011; Costa et al., 2014; Krishania et al., 2013).

The alkaline pretreatment is typically used in lignocellulosic materials with a high lignin content, such as wheat straw and sugarcane bagasse (Rabelo et al., 2011; Taherdanak and Zilouei, 2014). Alkaline pretreatments performed with bases such as sodium, potassium, calcium and ammonium hydroxides are effective in modifying the structure and solubilizing the lignin. In addition, the alkaline pretreatment reduces the degree of inhibition in methane fermentation and provides a lower cost of production (Ferreira et al., 2013; Krishania et al., 2013).

The use of an oxidizing compound in combination with an alkaline pretreatment is becoming more common in order to improve the digestibility of crop residues, compared with an alkaline pretreatment (Rabelo et al., 2011; Talebnia et al., 2010). The process is usually carried out at mild temperatures, using hydrogen peroxide (H_2O_2) and NaOH, leading to a lesser formation of inhibitors than in other processes.

The determination of the kinetic of the anaerobic digestion provides important information about the effect of the inhibitory compounds generated by the pretreatment on the biodegradability, and to determine if the hydrolysis is the limiting step. There are several models of the kinetic analysis of biogas production process; it all depends on the types of substrate used for anaerobic digestion and the controlling step.

The Gompertz model is well known among the available models for the kinetic behavior of the anaerobic digestion process considering inhibition. The Gompertz equation is used to estimate the kinetic parameters; biogas yield potential, duration of the lag phase, and maximum biogas production rate (Krishania et al., 2013). However, when the hydrolysis reaction is the rate limiting step of the overall process, as in the anaerobic degradation of some lignocellulosic substrates, the first order model is commonly used to estimate the extent of the reaction, and the hydrolysis constant. Both parameters can be used in a global model of the anaerobic digestion process (such as ADM1) to predict the performance of anaerobic digesters (Ferreira et al., 2013).

The present study aims to establish the influence of four pretreatments (thermal autoclaving, dilute HCl autoclaving, dilute NaOH autoclaving and alkaline peroxide) in the production of biogas from sugarcane bagasse and wheat straw, and to study the kinetics of anaerobic digestion in order to determine the influence of inhibitory compounds present in both the liquid phase and the solid phase.

2. Methods

2.1. Materials

Two lignocellulosic substrates were used in this study: WS, provided by the Castilla & León Institute of Technological Agriculture from Valladolid (Spain), and SCB (surplus after milling in a sugar/ethanol factory), donated by Usina Vale, City of Onda Verde-SP (Brazil). Wheat straw and sugarcane bagasse were washed for particulate material removal, dried in a ventilated oven at 42 °C and ground in an agricultural crusher to a size of 3–5 mm. Both substrates were kept in an oven at 45 °C until they reached a constant weight prior to compositional analysis and different pretreatments. The chemical composition of both substrates is presented in Table 1.

2.2. Pretreatments

Four different pretreatments were applied to both substrates in this study: thermal autoclaving (A), dilute HCl autoclaving (B),

Table 1
Composition of raw materials.

Parameter	Wheat straw	Sugarcane bagasse
Total solids (g TS/kg)	916.24 ± 1.21	919.22 ± 0.84
Volatile solids (g VS/kg)	818.83 ± 1.52	907.96 ± 1.10
N-TKN (g N/kg)*	4.85 ± 0.09	2.51 ± 0.02
TCOD (g O_2/kg)*	1150.40 ± 4.99	1188.85 ± 2.43
Cellulose (% w/w)*	35.19 ± 0.29	46.21 ± 0.10
Hemicellulose (% w/w)*	22.15 ± 0.21	20.86 ± 0.05
Total lignin (% w/w)*	22.09 ± 0.80	22.67 ± 0.04
Acid insoluble lignin (% w/w)*	18.17 ± 0.21	19.53 ± 0.03
Ash (% w/w)*	7.49 ± 0.29	1.19 ± 0.10

* Dry basis calculated composition.