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Influence of thermal pretreatment on the biochemical methane potential of wheat straw

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HIGHLIGHTS

- Influence of thermal pretreatment on the anaerobic biodegradation of wheat straw.
- Evaluation through BMP tests and modeling.
- Optimum severity factor at 220 °C and 1 min (3.5 severity factor).
- First order model confirmed that the hydrolysis is the limiting step.
- Surface response evaluation indicated negligible interaction temperature–time.

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ABSTRACT

The biochemical methane potential of steam exploded wheat straw was evaluated in a pilot plant under different temperature–time combinations. The optimum was obtained for 1 min and 220 °C thermal pretreatment (3.5 severity factor), resulting in a 20% increase in methane production respect non-treated straw. For more severe treatments the biodegradability decreased due to a possible formation of inhibitory compounds. The results of the tests were modeled with a first order equation to estimate the hydrolysis constant and biodegradability extent, and the influence of temperature and time on the kinetic parameters was obtained with a response surface study. The data processing confirmed the accuracy of the model and the optimum operation conditions, and demonstrated that the biomethanization of raw and pretreated wheat straw is limited by the hydrolysis, being the individual influence of temperature and time much more important than the interaction between them.

1. Introduction

In many countries, lignocellulosic materials are an abundant agricultural residue which can be used either for animal feeding or for energetic valorization in power plants. In Europe, wheat straw represents the largest agricultural waste, being in Spain an important part of the crop wastes which could be used as biomass for renewable energy production. The use of renewable energy sources is becoming increasingly necessary in order to cope with the impacts of global warming. The conversion of biomass into energy can be achieved in a number of ways, being anaerobic digestion a very sustainable alternative.

Anaerobic digestion is a well-known process for the treatment of wastewater of organic wastes. This process presents advantages over some conventional aerobic technologies, such as the better handling of wet waste, the production of biogas as a renewable source of energy and the attenuation of odor problems (Palmowski and Muller, 2000; Pérez-Elvira et al., 2011, 2010). Furthermore, anaerobic digestion is the most cost-effective treatment, due to high energy recovery and low environmental impact (Mata-Alvarez et al., 2000). However, the application of anaerobic digestion with lignocellulosic biomass has not been a subject of enough research.

Lignocellulosic material is mainly composed of three different types of polymers: cellulose, hemicellulose and lignin. While cellulose has a rigid and crystalline form, hemicellulose has a lower molecular weight and short lateral chains, which corresponds to an easy hydrolysable polymer. The third compound, lignin, is one of the most abundant polymers in nature. It is a complex and amorphous heteropolymer consisting of three different phenylpropane units, and is also non-water soluble (Hendriks and Zeeman, 2009). Wheat straw consists mainly of cellulose (30–40%), hemicellulose (20–30%) and lignin (10–20%). The cellulose and hemicellulose

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fractions can be enzymatically hydrolyzed to monomeric sugars after a pre-treatment aiming to hydrolyze its partially crystalline structure (Puls and Schuseil, 1993).

The hydrolysis of this type of biomass is limited by several factors, such as the lignin content. In cellulose the molecules are linear, and therefore they can form hydrogen bonds between the chains that limit their solubility in water, and reduce the available surface area, making cellulose difficult to degrade. A number of pretreatments for ligmocellulosic biomass are currently available, such as mechanical, milling into smaller pieces (Mshandete et al., 2006; Palmowski and Muller, 2000), physico-chemical such as dilute alkaline pretreatment (McIntosh and Vancov, 2011) or dilute acid pretreatment (Schell et al., 2003), wet oxidation, thermal treatment (Sapci, 2013), or a combination of them (Linde et al., 2008; Nkemka and Murto, 2013). From the point of view of its applicability, the total energy balance of the global process (considering both pre-treatment and digestion) must be taken into consideration. Compared to other pretreatment methods, the thermal hydrolysis can be cost effective if a proper steam-explosion and energy recovery is performed. The warranty that the process is energetically self-sufficient is described in Pérez-Elvira and Fdz-Polanco (2012). Furthermore, hydrothermal treatment can be performed without addition of chemicals or oxygen, representing a potential solution for the pretreatment of large quantities of lignocellulosic biomass including woods material (Horn et al., 2011a; Sipos et al., 2010) and agricultural by-products (Horn et al., 2011b; Ohgren et al., 2006).

Thermal pretreatment is a method where the substrates are subjected to heating under a specific pressure during a certain period of time. At the end of the heating, a steam explosion occurs, where the biomass is rapidly discharged into normal pressure causing an explosion of the macromolecules. At temperatures in the range 150–180 °C, parts of lignocellulosic materials will start to solubilize (Garrote et al., 1999). Some studies have shown that the effect of the thermal treatment depends on several factors, such as: residence time, operating temperature, chip size, and moisture content (Bauer et al., 2009; Han et al., 2010; Zhang et al., 2008). A too harsh treatment of lignocellulosic biomass may result in a lower methane yield and longer retention time. The reason is that when lignin is broken, there is a risk of formation phenolic and hererocyclic compounds from hemicellulose and cellulose degradation, like furfural and hydroxymethylfurfural (HMF), which are known to inhibit many fermented microorganisms, including those involved in the biogas generation (Hendriks and Zeeman, 2009). According to Raj (2009) the concentration of furfural that inhibits methanogens ranges from 2400 to 3000 mg/L.

The aim of this research is to study the impact of thermal hydrolysis on the biodegradability of wheat straw under mesophilic anaerobic conditions, by using an experimental approach and mathematical modeling of the results. The final applicable objective is to define the pretreatment parameters that optimize the methane productivity.

2. Methods

2.1. Raw material

Wheat straw was grown in Valladolid (Spain) and harvested in 2011. For all the experiments, the straw was cut into pieces of 10 cm long. The average values obtained in wheat straw characterization are: 922 ± 2 g TS/kg (92%VS/TS), 1078 ± 8 g TCOD/kg, 4.72 g N-TKN/kg, and a ratio C/N around 92.

2.2. Thermal pre-treatment pilot plant and operation conditions

The Cambi® thermal treatment plant, steam explosion unit, consists of a 30 L reactor and a flash tank with a removable bucket to collect the pretreated material (Fig. 1). The steam is generated by a 25 kW electric steam boiler (200 L capacity) which can supply steam up to a maximum pressure of 34 bar (240 °C). Wheat straw is loaded into de reactor using a motorized (M) ball valve (V4) at the top of the reactor. Steam is added to the reactor from the bottom, through an air-actuated valve (V1), heating the waste during the time established. The desired operation pressure (corresponding to a certain temperature) is set on the control panel unit, controlled automatically by the air-actuated valve (V1). For security reasons also a manual valve (V2) has to be opened to add steam to the pressure reactor. An air-actuated ball valve at the bottom of the vessel (V3) is responsible for the rapid pressure drop (explosion) and release of the pretreated biomass to the flash tank. The pretreated biomass is collected in a removable bucket at the bottom of the flash tank. The steam that is leaving the flash tank is condensed and led to a water tank (WT). Any steam that is not condensed leaves the unit via a carbon filter (CF) to remove smell.

Different pre-treatment conditions were tested varying both temperature (ranging 150–220 °C) and time (ranging 1–15 min). In all the experiments, one kilogram of wheat straw was used. The reactor was preheated for about 15 min at the same temperature selected for the pre-treatment before starting the experiments.

Temperature and time determine the severity factor of the treatment. This parameter ($\log R_0$, Eq. (1)) is most widely accepted for steam pre-treatments (Hendriks and Zeeman, 2009) to express the severity of the pre-treatment:

$$\log R_0 = \log\left(t \cdot \exp\left(\frac{T - 100}{14.75}\right)\right) \quad (1)$$

where t is the time (min), T the temperature (°C), 100 is the base temperature (100 °C), and 14.75 is the activation energy based on the assumption that the reaction is hydrolytic and the overall conversion is first order (Xu et al., 2011). This expression only takes into account time and temperature, and does not consider the effect of the flash. The study of this effect is not assessed in this paper.

Theoretically, the more severe a treatment is, the more cellulose is made available for digestion. However, very severe pre-treatments can lead to formation of inhibitory compounds from the macromolecules, driving to an indirect relationship between the severity factor and the biodegradability. Therefore there should be an optimum value for the severity factor.

2.3. Anaerobic biodegradability

Batch anaerobic digestion tests (BMP) were carried out in triplicate to assess the wheat straw biodegradability after the different pre-treatment conditions applied. A control test without substrate and a control with cellulose were included in order to check the methanogenic activity of the inoculum. All the experiments were carried out at mesophilic conditions in a thermostatic room (35.1 ± 0.3 °C), with constant mixing in a rotary desk.

The anaerobic inoculum used for the batch test was taken from a pilot-scale mesophilic anaerobic digester treating mixed sludge from a municipal wastewater treatment plant, with a volatile solids (VS) concentration of 12 gVS/kg. The inoculum was pre-incubated for four days (35.1 ± 0.3 °C) in order to minimize its residual biodegradable organic material content.

Bottles of 2 L volume were used, made of borosilicate glass (260 mm height, 160 mm diameter and a 40 mm bottleneck), placed horizontally in a rotary table to achieve a good mixing.