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The use of thermochemical pretreatments to improve the anaerobic biodegradability and biochemical methane potential of the sugarcane bagasse

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HIGHLIGHTS

- Enhancing anaerobic biodegradability of sugarcane bagasse using pretreatments.
- Delignification for improving biochemical methane potential of sugarcane bagasse.
- Production of renewable energy via anaerobic digestion of sugarcane bagasse.
- Sugarcane bagasse pretreatment optimisation by using response surface methodology.

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ABSTRACT

Lignocellulosic material can be used as biomass for power generation via biogas if it is pretreated to improve the anaerobic hydrolysis step, by either solubilising the hemicellulose (total reducing groups, TRG) or removing lignin (Lig), with consequent exposition of the cellulose fibre to anaerobic degradation. We evaluated the effects of acid, alkaline, and hydrothermal pretreatments on sugarcane bagasse to increase its anaerobic biodegradability and biochemical methane potential (BMP). The highest sugar production (31.14 g TRG/g substrate) was achieved with the acid pretreatment in 6.4 min at 138 °C, with a HCl concentration of 0.63 M, and the highest lignin removal (23.24 g Lig/g substrate) was found with the alkaline pretreatment after 47 min at 184 °C and a NaOH concentration of 0.8 M. However, the best values of BMP (197.5 L CH_4/kg substrate) and anaerobic biodegradability (27.4%) were achieved by the hydrothermal pretreatment after 10 min at 200 °C, which was sufficient to generate power of 6.8 MJ/kg substrate. The results showed that the methane derived from the anaerobic digestion of these hydrolysates produced less energy than the direct burning of the dry bagasse. Thus, the recovered lignin, with its high added-value, may be used to improve environmental sustainability and profitability of the process. In this case, the alkaline pretreatment extracted 80.2% of the lignin present in the bagasse, and the hydrolysate could generate 313.4 L CH_4/kg substrate.

1. Introduction

Sugarcane bagasse is the lignocellulosic by-product generated in the sugar and ethanol industry during sugarcane juice extraction. Bagasse is commonly used as a fuel in boilers that produce low pressure steam [1]. However, not all produced bagasse is used and the surplus that remains leads to environmental and storage problems [2]. The total sugarcane production in Brazil for the 2012–13 harvesting period is estimated to be 596.6×10^6 t [3],

Abbreviations: COD, chemical oxygen demand; DNS, 3,5-dinitrosalicylic acid; HMF, 5-hydroxymethylfurfural; HPLC, high performance liquid chromatography; LHV, lower heating value; Lig, lignin; BMP, biochemical methane potential; SMA, specific methanogenic activity; TRG, total reducing groups; VS, volatile solids.

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with the bagasse-generation rate of approximately 0.135 t/t sugarcane [4]. Therefore, Brazil will generate approximately 80.5×10^6 t of bagasse by the end of year 2013. The conversion of the bagasse generated during the above mentioned period would result in the production of up to 32×10^9 m^3 biogas. Considering that biogas contains 60% methane and has a lower heating value (LHV) of 34 450 kJ/m^3 [5], this lignocellulosic by-product could generate theoretically 1.1×10^9 GJ of energy.

Sugarcane bagasse fibre consists of cellulose (25–47%), hemicellulose (20–35%), and lignin (15–35%) [2,6,7]. Cellulose and hemicellulose can be converted into methane via anaerobic fermentation, producing energy and increasing the energy potential of the sugar and ethanol industry. However, to maximise energy production by anaerobic digestion, it is necessary to consider the limiting step of the process, hydrolysis [8]. In general, during the anaerobic digestion of lignocellulosic material, the complex organic polymer components initially undergo hydrolysis, via enzymatic decomposition, into monomers such as sugars and organic acids. However, the cellulose and hemicellulose fractions in the lignocellulosic material are surrounded by lignin, which acts as a physical barrier and hinders anaerobic degradation. In this case, a pretreatment method may remove the lignin fraction. Furthermore, the hemicellulose fraction itself acts as a physical barrier to the enzymatic attack of the cellulose. In this case, pretreatment must solubilise the hemicellulose fraction into sugars, allowing the hydrolysis of the cellulose and consequently increasing anaerobic biodegradation [9].

Different factors affect the biodegradability of lignocellulosic materials: cellulose crystallinity, accessible surface to enzymes, structure and distribution of lignin [10–12]. Inter- and intramolecular hydrogen bonds maintain the crystalline regions and make the cellulose resistant to acid, alkaline, or enzymatic hydrolysis. Furthermore, the crystalline regions make cellulose water insoluble, which hinders biodegradation [13]. The resistance to enzymatic degradation of the lignocellulosic material is also influenced by the lignin content and distribution. This hydrophobic polymer forms an interlaced network [14], which decreases the accessible surface and prevents the cellulolytic enzymes attack [15,16], slowing or preventing the anaerobic hydrolysis [17]. Therefore, the delignification process can improve the anaerobic biodegradation [9,10] and may represent a good prospect for lignin recovery which is a high value-added by-product.

The most-used physical pretreatment is milling, which decreases the crystallinity and degree of polymerisation of the cellulose [10]. However, depending on the structure and composition of the biomass (cellulose, hemicellulose and lignin content), as well as on the use of the pretreated material (ethanol, biogas or lignin production), it is necessary a further treatment, which includes: (i) acid hydrolysis (using dilute or concentrated acid), in which part of the cellulose and hemicellulose is converted into fermentable sugars [9]; (ii) hydrothermal hydrolysis, wherein the hemicellulose is solubilised and produces acetic acid that acts as a catalyst for the reaction [18], with further reduction of the polymerisation degree that leads to an increase in sugar yield [19]; (iii) alkaline hydrolysis, typically used in lignocellulosic materials with high lignin content [20–22], that promotes the lignin solubilisation, improves the reactivity of the remaining polysaccharides, removes acetyl groups and various uronic acid substitutions of the hemicellulose [23], swells the material, increases the porosity, and consequently increases the surface accessibility for exoenzymes [2,24]; and (iv) enzymatic hydrolysis, catalysed by a complex composed of various enzymes such as cellulase, hemicellulase, β-glucosidase, xylanase, arabinase, and pectinase [25–27]. The latter method is often used in conjunction with other types of pretreatments to reduce the physical barriers presented by lignin prior to the enzymatic attack.

Several other advanced pretreatment methods for delignification or sugar production from sugarcane bagasse have been investigated: addition of subcritical or supercritical CO_2 to form weak acid catalyst with water [28,29]; ultrasonic cavitation for increasing accessible surface for enzyme attack [30–32]; microwave-based heating for increasing the reaction temperature [33,34]; organosolv delignification [35,36]; lignin degradation by ozone and singlet oxygen produced by plasma [37,38], ammonia fibre expansion for increasing accessible surface and cleavage of the ether bonds of lignin [39,40]; disruption of the inter- and intramolecular hydrogen bonds of cellulose by ionic liquid [41,42]. However, most of the researches on pretreatment of sugarcane bagasse focus on 2nd generation ethanol, which is mainly based on the fermentation of hexoses by *Sacaromices cerevisiae*. On the other hand, the methanogenic consortia can hydrolyse cellulose and hemicellulose, producing sugars and organic acids that will be further converted into methane. Therefore, the pretreatment can be less aggressive or severe, with less input of energy and chemicals, just enough to increase the extracted lignin, to decrease crystallinity and to increase surface accessibility.

This study evaluated several pretreatments applied to sugarcane bagasse to maximise its anaerobic biodegradability, and hence, its biochemical methane potential (BMP). Prior to the anaerobic digestion assays, the bagasse was subjected to hydrothermal pretreatment, acid hydrolysis with dilute hydrochloric acid, or alkaline hydrolysis with sodium hydroxide solution. Each pretreatment was optimised based on temperature, reaction time, and catalyst concentration by applying multivariate factorial design and response surface methodology.

2. Material and methods

2.1. Sugarcane bagasse source

The sugarcane bagasse was provided by an ethanol plant located in Pernambuco, Brazil. Because of its high moisture content, the by-product material was frozen at −20 °C and then lyophilised, milled in a knife mill, sieved (18 mesh, 1 mm), homogenised, and stored at room temperature. Prior to carrying out the three pretreatments, the cellulose, hemicellulose, and lignin contents of the bagasse were characterised (38.7% cellulose, 33.0% hemicellulose, 25.7% lignin, and 2.6% ash and extractives).

2.2. Experimental design and statistical analysis

All hydrolysis assays were performed using 2^2 and 2^3 multivariate experimental designs (two levels and two or three independent variables, depending on the pretreatment), with the central point in triplicate (level 0) and four or six star-points (when necessary), as shown in Table 1. Concentrations of acid or base, reaction time, reaction temperature, and, in the case of hydrothermal pretreatment, the bagasse-mass-to-catalyst-solution-volume ratio, were the independent variables. The P_{TRG} and P_{Lig} were the dependent variables.

The interrelationship between dependent and independent variables was calculated using linear, quadratic and interaction effects. The equations of the response surface were calculated by multiple linear regressions using the least squares methodology. Statgraphics® Centurion XV (StatPoint, USA) was used for statistical analysis and response surface modelling.

2.3. Hydrolysis assays

The hydrolysis assays were conducted in 500 mL high-pressure reactors (Berghof, model BR-300). In all the tests, the ratio of the