# Optimization of sugarcane bagasse autohydrolysis for methane production from hemicellulose hydrolyzates in a biorefinery concept
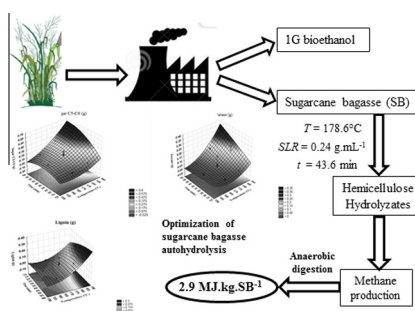
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## HIGHLIGHTS

- SB autohydrolysis was optimized by experimental design to produce methane.
- Milder AH condition (178.6 °C; 43.6 min; $SLR = 0.24$) was the best for $CH_4$ production.
- $CH_4$ production was 1.56 $Nm^3$ $CH_4$ kg $TOC^{-1}$ which could potentially generate 2.9 MJ kg $SB^{-1}$.

## GRAPHICAL ABSTRACT

## ABSTRACT

This study aimed to optimize through design of experiments, the process variables (temperature – $T$, time – $t$ and solid-to-liquid ratio – $SLR$) for sugarcane bagasse (SB) autohydrolysis (AH) to obtain hemicellulose hydrolyzates (HH) prone to anaerobic digestion (AD) and biochemical methane production (BMP). The results indicated that severe AH conditions, which lead to maximum hemicelluloses dissolution and sugar content in the HH, were not the best for BMP, probably due to the accumulation of toxic/recalcitrant compounds (furans and lignin). Mild AH conditions (170 °C, 35 min and $SLR = 0.33$) led to the highest BMP (0.79 $Nm^3$ kg $TOC^{-1}$), which was confirmed by the desirability tool. HH produced by AH carried out at the desired condition DC2 (178.6 °C, 43.6 min and $SLR = 0.24$) showed the lowest accumulation of inhibitory compounds and volatile fatty acids (VFA) and highest BMP (1.56 $Nm^3$ kg $TOC^{-1}$). The modified Gompertz model best fit the experimental data and led to a maximum methane production rate ($R$) of 2.6 mmol $CH_4$ $d^{-1}$ in the best condition.

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## 1. Introduction

All around the world, a great quantity of energy comes from fossil fuels. It is known that such resources are non-renewable and that their quantity at the Earth's crust remains uncertain.

The world's oil reserves require good management to ensure its longevity. In addition, geopolitical risks from dependence on oil by politically unstable countries, and major commitments made to the environment have drawn greater attention to the use alternative energy sources. Resultingly, the use of renewable sources for energy production has been strongly encouraged worldwide (Cherubini and Jungmeier, 2009).

The most common source of renewable fuel produced worldwide is bioethanol, which is usually obtained from corn (starch),

sugar beet (sucrose), and sugarcane (sucrose). In this context, Brazil has occupied a prominent place along with the United States regarding the production of bioethanol from sugarcane juice and cornstarch (Soccol et al., 2010).

Other sources of renewable raw materials widely studied for conversion into biofuel and biogas are the lignocellulose residues. The production of liquid or gaseous biofuels and value-added byproducts from wasted lignocellulosic biomass have highly favorable environmental aspects (Sanchez and Cardona, 2008). Every year, large quantities of lignocellulosic wastes accumulate worldwide due to the agricultural and agro-forestry production. Often, the allocation of these materials is not entirely noble, represents a loss of their energy production potential, besides posing environmental issues. In this context, Brazil assumes a prominent position, when considering the volume of agricultural and agro-forestry production in the country and the consequent generation of lignocellulose residues. Such residual biomasses are available in a reasonably clean form and in large amounts (Pandey et al., 2000).

Among the agricultural wastes generated in large amounts in Brazilian territory, one should highlight that sugarcane bagasse (SB), is a waste generated during the production of first generation (1G) bioethanol in sugarcane mills. It is estimated that the sugarcane crop during 2015/2016 season has reached 663 million tons (CONAB, 2015). Considering that approximately 250–280 kg of SB is generated by 1.0 ton of processed sugarcane, it is proposed that the Brazilian sugar and alcohol sector has reached 166–186 million tons of bagasse during 2015/2016 season (Rocha et al., 2015).

Currently, in Brazil, the majority of SB is used to meet the energy demands in alcohol/sugar plants. It is estimated that the amount of energy produced by its burning to produce steam exceeds by twofold, the amount of energy required for sugar and alcohol production (Costa et al., 2014). Therefore, part of the residual SB is not energetically harnessed. A complete use of this SB is extremely desirable from both economically and environmentally points of view; and, its chemical composition makes it an interesting industrial raw material of strategic economic importance.

The peculiar characteristics of SB, particularly the large amount of carbohydrates in the form of hemicelluloses and cellulose, have encouraged research on bioconversion processes of this material for the production of second generation (2G) bioethanol, biogas ($CH_4$ and $H_2$) and other bioproducts (Batalha et al., 2015; Costa et al., 2014). In fact, some authors do not consider SB a byproduct or residue of the sugar and alcohol industry, but instead as a high value co-product, which can be used as a raw material for the production of biofuels and bioproducts (Pandey et al., 2000).

Generally speaking, lignocellulosic biomass is a natural, cheap and abundant source that can be exploited for the production of biofuels and bioproducts. SB, particularly, is mainly composed of cellulose (30–45%), hemicelluloses (25–30%) and lignin (25–30%), which account for about 90% of its dry weight (Badshah et al., 2012). However, the complex interactions between these three main components (cellulose, hemicelluloses and lignin) in the cell wall propose the main challenge for the biotechnological use of lignocellulose residues such as sugarcane bagasse (Sun, 2004). As a result, the development of processes for the conversion of such residues into biofuels should involve an integrated optimization of the type of lignocellulose biomass, chemical characterization and pretreatment needs (Gouveia et al., 2009).

Generally, the methods for lignocellulosic biomass pretreatments can be grouped into different categories: physical, physico-chemical, biological and chemical. The hydrothermal pretreatment, also known as autohydrolysis (AH) pretreatment, has been studied by different researchers (Batalha et al., 2015; Santucci et al., 2015) as a step prior to enzymatic hydrolysis of SB to increase enzymes accessibility and thereby cellulose conversion to C-6 sugar (glucose). Consequently, this could be further used as a substrate for 2G bioethanol production via yeast fermentation.

During AH pretreatment, water molecules penetrate the biomass, promoting cellulose hydration, hemicelluloses dissolution, and slight lignin removal. AH pretreatment is highly effective in increasing the accessibility and susceptibility of cellulose surface area, thereby enhancing its biodegradability and enzymatic conversion. AH pretreatment has the potential of improving monomeric sugars extraction, pentoses recovery and cellulose degradability, with the advantage of producing a hydrolyzate with lower concentration of toxic compounds, such as 2-furfuraldehyde (FF) and 5-hydroxymethyl-2-furfuraldehyde (HMF), when compared to acidic or steam explosion pretreatments (Zheng et al., 2014).

Moreover, AH pretreatment of SB leads to the production of a hemicellulose hydrolyzate rich in pentose sugars (mainly xylose and arabinose), which cannot be easily converted into bioethanol via biochemical processes (Kaparaju et al., 2009). The use of hemicellulose hydrolyzate for the production of 2G bioethanol normally requires the development of genetically modified microorganisms that could thrive on pentose. A process that enables the application of such microorganisms on an industrial scale, however, has not yet been developed (Rabelo et al., 2011).

Another alternative to harvest the energy of hemicellulose hydrolyzates is the production of biomethane via anaerobic digestion (AD). Such an alternative may be part of an energy-viable and sustainable solution for integrating 1G and 2G bioethanol production processes in the sugar and alcohol industries. The biomethane could be an additional source of energy to partially replace sugarcane bagasse as a fuel in cogeneration systems. Furthermore, the use of biomethane produced from anaerobic digestion of hemicellulose hydrolyzates opens the possibility of integral use of the SB in the lignocellulose biorefinery. The remaining cellulose-rich solid fraction generated after hemicellulose extraction could be further used for 2G bioethanol production.

Most of the studies available in the literature consider the whole use of pretreated biomass, i.e. solid and liquid fractions, to produce $CH_4$ and evaluate the effects of pretreatment in the digestibility of SB when compared to raw SB. The use of whole pretreated material for methane production hinders the rational and efficient use of all biomass fractions, such as the destination of the cellulose-rich solid fraction for 2G bioethanol production. Therefore, this study aimed to evaluate the AH pretreatment of SB in order to obtain hemicellulose hydrolyzates adequate for biomethane production via classic anaerobic digestion. In addition, the present study tests the hypothesis that the optimization of AH conditions cannot be solely based on the sugar content in the hydrolysates if methane production is the main goal.

Special attention has been given to the use of high values of *SLR*, which were evaluated aiming to decrease the water consumption in the AH pretreatment. The biomethane production via AD of hemicellulose hydrolyzates was also intensively studied and optimized through a Doehlert experimental design and desirability tool of Statistica® software. The potential for power generation using biomethane in a biorefinery concept using the best scenario found in this study was also estimated.

## 2. Methods

### 2.1. Chemicals

Cyclohexane and ethanol (99.5%) were purchased from Synth (Brazil). Sulfuric acid (95–98%) was purchased from Synth (Brazil). The chromatography–grade standards cellobiose, D-glucose, D-xylose, L-arabinose, acetic acid, formic acid, propionic, isobutyric,