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Hydrodynamic cavitation-assisted alkaline pretreatment as a new approach for sugarcane bagasse biorefineries

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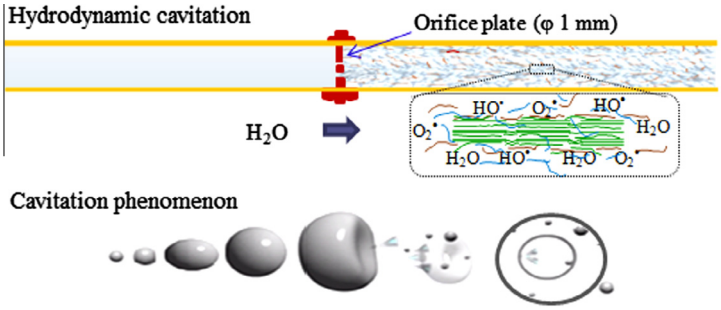
HIGHLIGHTS

- Hydrodynamic cavitation (HC) was combined with an alkaline pretreatment.
- HC-assisted pretreatment was statistically optimized and experimentally verified.
- High enzymatic digestibility of 97.2% was achieved.
- The HC increased enzymatic digestibility by 30%.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrodynamic cavitation (HC) was employed in order to improve the efficiency of alkaline pretreatment of sugarcane bagasse (SCB). Response surface methodology (RSM) was used to optimize pretreatment parameters: NaOH concentration (0.1–0.5 M), solid/liquid ratio (S/L, 3–10%) and HC time (15–45 min), in terms of glucan content, lignin removal and enzymatic digestibility. Under an optimal HC condition (0.48 M of NaOH, 4.27% of S/L ratio and 44.48 min), 52.1% of glucan content, 60.4% of lignin removal and 97.2% of enzymatic digestibility were achieved. Moreover, enzymatic hydrolysis of the pretreated SCB resulted in a yield 82% and 30% higher than the untreated and alkaline-treated controls, respectively. HC was found to be a potent and promising approach to pretreat lignocellulosic biomass.

1. Introduction

Sugarcane bagasse (SCB) is an important feedstock for cellulosic ethanol production in many countries and particularly so in Brazil (Clauser et al., 2015). SCB, a lignocellulosic biomass, is composed of carbohydrates (cellulose and hemicelluloses), lignin, and other minor components as extractives and inorganic compounds (Vallejos et al., 2015). All these components are intertwined via lignin acted as glue in an exceedingly complex way, rendering the whole material strong and recalcitrant to biological degradation (Benjamin et al., 2013; Terán-Hilares et al., 2016). It is this reason that lignocellulosic has to go through pretreatment to be able to be susceptible to enzymatic hydrolysis (Raghavi et al., 2015; Kim et al., 2015). Examples of such pretreatment methods include ammonia fiber explosion, hydrothermal treatment, acid or alkaline treatment, ultrasound and microwave irradiation (Kim et al., 2013; Angarita et al., 2015).

Hydrodynamic cavitation (HC) is one potential option, because the HC-assisted process is known to possess advantages of high

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energy-efficiency and scaling-up easiness in comparison to a popular and powerful method ultrasound (US), and also to reduce the use of chemical catalysts, still with high lignin removal and high glucose yield (Sharma et al., 2008; Kim et al., 2015).

In the HC, cavitation is generated by pressure variation in a flowing liquid, which can be caused by constriction (venture nozzles, orifice plates or throttling valve). When a liquid passes through the constriction, a number of micro-bubbles (vapor cavities) are formed due to a decrease in pressure below the vapor pressure of the liquid. Subsequently, the micro-bubbles collapse due to slowed flow and pressure recovery (Sharma et al., 2008; Gonçalves et al., 2014). This bubble collapse is strong enough to generate localized "hot spots" with transient temperatures of about 10,000 K, and pressure of about 1000 atm, which can induce chemical and physical transformations. Besides, water molecules are dissociated into chemical products, like hydroxyl radical ($OH^{\cdot}$) that is one of the most powerful oxidants and excellent initiator of chain reactions (Ozonek, 2012; Li et al., 2015). Another important effect is the generation of shock waves during violent collapse of cavities that also are responsible for pyrolysis/molecular breakdown of organic molecules trapped inside or in the vicinity of cavities (Saharan et al., 2013).

The mechanical means, despite its distinctive effectiveness, has limitedly been utilized especially for the purpose of biomass pretreatment. In this work, therefore, the HC was adopted and combined with alkaline pretreatment of sugarcane bagasse. Response surface methodology (RSM) was employed as a tool to find important variables and optimal conditions.

2. Materials and methods

2.1. Materials

Sugarcane bagasse was obtained from Usina São Francisco (Sertãozinho-SP, Brazil). The biomass was air-dried and milled in a Benedetti 270 hammer mill (Mill Benedetti Ltda, Pinhal-SP, Brazil). The milled bagasse was classified using standard Tyler sieves (10 and 14 mesh) and powders with particle sizes between 1.18 and 1.70 mm were collected, stored at room temperature in a sealed container and used for this study. SCB was comprised of 40.6% glucan, 26.3% of xylan and 24.9% of lignin on dry weight basis.

2.2. HC-assisted alkaline pretreatment

Pretreatment of SCB was performed in a laboratory HC-system. The HC-system consisted of a reservoir and a stainless steel cylindrical cavitation reactor which were connected to a centrifugal pump with a power of 1.5 kW. A radial form of orifice plate with 27 holes of 1 mm diameter was used in all experiments (Kim et al., 2015). Pressures of upstream and downstream were kept at 0.3 and 0.03 MPa, respectively. In order to aid each particle in fully experiencing the cavitational effect, sugarcane bagasse was kept in a cylindrical wire cloth (40 mesh) that was placed within so-called cavitation zone in the cavitation reactor. Alkaline solution was passed through the cavitation zone continuously. Dry solid/liquid ratio (S/L) was calculated on the basis of the cavitation reactor volume of 100 mL.

For the sake of comparison, conventional alkaline and ultrasound-assisted pretreatment of SCB were also performed along with the optimal combination of HC assisted pretreatment parameters (as Section 2.6). The US-assisted pretreatment was carried out using a probe type ultrasonic processor (VCX 750, USA) at a power of 300 W (40% amplitude) and a frequency of 20 kHz.

After pretreatment, the solid fraction was washed, dried and characterized to determinate its main components as cellulose, hemicelluloses and lignin (Sluiter et al., 2011).

2.3. Enzymatic hydrolysis

Enzymatic hydrolysis experiments were carried out in a 125 mL Erlenmeyer flask containing 50 mM sodium citrate buffer solution (pH = 4.8) at 5% (w/v) solid loading. A novel enzyme blend Cellic C-Tec (Novozymes, Denmark) corresponding to 20 FPU/g of dry biomass was used in all experiments and saccharification was proceeded for 48 h (Bahrani et al., 2015). Hydrolyzates were withdrawn periodically and analyzed for sugar concentration by high performance liquid chromatography (HPLC) equipped with a HPX-87H column (Bio-Rad, USA) (Kim et al., 2015).

2.4. Scanning electron microscopy (SEM) analysis

Surface morphology of the pretreated SCB was characterized by Scanning Electron Microscope SU5000 (Tokyo, Japan) with acceleration voltage of 10 kV and working distance of around 50 μm, and compared with the untreated SCB (Chandel et al., 2014).

2.5. X-ray diffraction

Crystallinity index of the untreated and pretreated SCB was analyzed using XRD-600 diffractometer (Shimadzu, Tokyo, Japan). The X-ray diffractometer was set at 40 kV and 30 mA. Samples were scanned over the range of $2\theta = 5–50^{\circ}$ and the crystallinity index (CrI) was determinate using Eq. (1) (Segal et al., 1959).

$$\mathrm{CrI}\ (\%) = \left[(\mathrm{I_{Crystalline}} - \mathrm{I_{Amorphous}})/\mathrm{I_{Crystalline}}\right] \times 100\% \quad (1)$$

where $I_{crystalline}$ = Intensity at 22.3° and $I_{amorphous}$ = Intensity at 16.1°

2.6. Experimental design

Response surface methodology (RSM) was used to optimize the HC-assisted alkaline pretreatment aiming at high glucose yield. Three independent variables, NaOH concentration (X_1), solid/liquid ratio (X_2) and reaction time (X_3), were studied. The ranges of pretreatment conditions were established as follows: NaOH concentrations of 0.1–0.5 M, solid/liquid ratios of 3–10%, and reaction times of 15–45 min. A total of 15 experimental trials of the three variables were designed by Box–Behnken design using the Design-Expert software 8.0 (Stat-Ease, Inc., USA) (Box and Behnken, 1960).

3. Results and discussion

3.1. Hydrodynamic cavitation-assisted alkaline pretreatment

Solid recovery after pretreatment was found to fall between 74.2% and 86.5%, and the maximal lignin removal (54.6%) was observed when the pretreatment was done at 0.5 M of NaOH, 6.5% solid/liquid ratio and 45 min of HC time (No. 8; Table 1).

The response variable lignin removal was adjusted by a two factor interaction (2FI) model ($R^2 = 0.945$) and the significance of each coefficient on the lignin removal was evaluated by p-value (lower then 0.01) and F-value (42.82); all this indicated a high statistical significance of the model, which is shown in the Eq. (2) in terms of actual values of the studied variables. In this model, only significant terms (p-value < 0.05) were considered. Under a pretreatment condition of 0.48 M of NaOH, 4.24% S/L ratio and 44.48 min of process, the maximal lignin removal predicted by the model