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Full Length Article

Acid post-hydrolysis of xylooligosaccharides from hydrothermal pretreatment for pentose ethanol production

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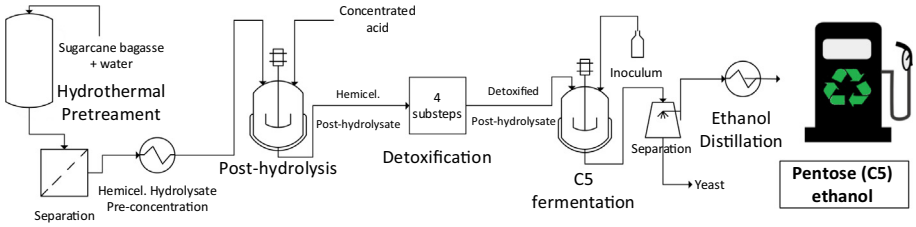
HIGHLIGHTS

- The acid post-hydrolysis of a hydrothermal hemicellulosic hydrolysate was studied.
- The performances of three acids: oxalic, maleic and sulfuric acid was compared.
- The C5-rich post-hydrolysates were fermented with a wild-type yeast.
- Sulfuric acid showed the best kinetic of post-hydrolysis of xylooligosaccharides.
- Acid post hydrolysis increases overall ethanol yield from sugarcane bagasse.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrothermal pretreatment solubilizes about 65% of the hemicelluloses in sugarcane bagasse. However, nearly 80% of the xylose recovered from the hemicellulosic hydrolysate is present as xylooligosaccharides (XO's), which cannot be directly fermented into pentose (C5) ethanol. In this work a kinetic study of the post hydrolysis process considering the use of three acids – sulfuric, oxalic and maleic – was performed. Xylose and furfural post-hydrolysis profiles showed the reaction time in which xylose peaked with minimum furfural production. Among the three studied acids, sulfuric acid showed the fastest kinetics of post-hydrolysis with XO's being fully hydrolyzed in less than 1 h reaction time. C5 fermentation experiments showed that the detoxified post-hydrolysates fermented with ethanol yields ranging from 0.10 to 0.31 g ethanol g^{-1} reducing sugars. Most samples were fermented from 48 to 72 h of experiment with productivities ranging from 0.02 to 0.43 g $\cdot L^{-1} \cdot h^{-1}$.

1. Introduction

Although essential, biomass pretreatment is also an economic hurdle that greatly impacts the overall costs of other unit operations in the production of second generation (2G) ethanol. Hydrothermal pretreatment is a water-based and environment-friendly pretreatment that does not require addition of other reagents, reducing the consumption of chemicals for pH adjustment and the risk of equipment corrosion [23].

Hydrothermal pretreatment of sugarcane bagasse—Brazilian's main agricultural residue for ethanol production—solubilizes hemicelluloses down mainly to xylooligosaccharides (XO's), in addition to a small monomeric fraction, leading to less sugars

Abbreviations: DPH, detoxified post-hydrolysate; HH, hemicellulosic hydrolysate; HPH, hemicellulosic post-hydrolysate; XO, xylooligosaccharide.

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degradation and consequently less fermentation inhibitors generation [9]. However, XO's cannot be directly fermented by microorganisms. A post-hydrolysis of the hemicellulosic hydrolysate (HH) is required for the second generation (2G) ethanol production via the biochemical platform biorefinery concept [11]. Post-hydrolysis can be carried out via either chemicals or enzymes. XO's structure resemble its parent macromolecule, hemicelluloses, a highly branched and complex heteropolymer. A broad hemicellulolytic enzymes cocktail would be required to depolymerize XO's, increasing the process cost mainly due to longer residence times, which directly impact on the size of reactors, and making it economically unfeasible [7].

The acid post-hydrolysis of lignocellulosic hydrolysates from different biomasses has been widely reported in the literature. It was first employed by Saeman [25] to quantify the total hexose (C6) sugars in solid wood samples, and later adapted by Mok and Antal [22] for pentose sugars (C5) in HH's naming it Quantitative Saccharification. However, there is only one report in the literature on the post-hydrolysis of soluble XO's from sugarcane bagasse for 2G ethanol production so far [36].

Additionally, most of the post-hydrolysis studies for lignocellulosic materials were limited to a very small scale, either high throughput or small capacity tubes, in which problems related to mass transfer are barely seen [16,37,36]. Such studies proved the efficacy of post-hydrolysis but gave no further idea of possible challenges of process scale-up.

While it may seem contradictory using acid in the post-hydrolysis of HH's once the hydrothermal pretreatment was chosen precisely for its greener features, there are several advantages associated to the hydrothermal pretreatment followed by a post-hydrolysis in comparison to the diluted acid pretreatment:

i. The foremost fact is the rising attention hydrothermal pretreatment itself has been gaining. When compared with the diluted acid pretreatment, it is considered more environment-friendly and cheaper [5]. Besides avoiding hemicelluloses degradation, which may pave the way for a C5-utilization platform.
ii. In post-hydrolysis, smaller reaction volumes are used—only the HH—contrary to the whole biomass used in pretreatment. This avoids using additional amounts of acid needed to neutralize ashes in the whole biomass [18]. Therefore, the amount of acid used per liter of ethanol is lower.
iii. There's a heterogeneous medium in pretreatment due to an abrasive solid substrate—sugarcane bagasse. In post-hydrolysis there is a pseudo-homogeneous liquid medium [16] that allows higher mass transfer rates.
iv. Pretreatment is performed at higher process temperatures ($T \geqslant 190\ ^{\circ}C$), which together with the solid substrate may accelerate equipment wear out. On the other hand, post-hydrolysis occurs at lower temperatures ($120\ ^{\circ}C \leqslant T \leqslant 150\ ^{\circ}C$), which reduces process severity.

In this work, the post-hydrolysis performances of sulfuric, maleic and oxalic acids on sugarcane bagasse HH in a bench scale reactor (2 L) were compared. Maleic and oxalic acids were selected due to their selectivity to hydrolyze XO's, i.e. producing more xylose with less degradation into furfural when compared to sulfuric acid, as previously mentioned by Lu and Mosier [19].

Kinetic profiles of XO's post-hydrolysis, C5 monomers and furfural were determined. The post-hydrolysates were then fermented by *Scheffersomyces stipitis* (wild type yeast able to consume xylose) and compared in terms of ethanol yield and volumetric productivities. A quantitative insight into the pentose use in 2G ethanol production from sugarcane bagasse is therefore provided in this work.

2. Materials and methods

2.1. Feedstock

Sugarcane bagasse was provided by Usina da Pedra (Serrana – SP). The material was collected in the 2012/13 crop (May/2012). It was mechanically harvested and resulted from the last milling before juice extraction. Samples subjected to hydrothermal pretreatment were not comminuted. The chemical composition of raw sugarcane bagasse, as percentage of dry mass, was: cellulose, 41.38 ± 0.14%; hemicelluloses, 27.84 ± 0.50%; lignin, 22.50 ± 0.43%; extractives 4.01 ± 0.06% and ashes, 5.62 ± 0.45%.

2.2. Hydrothermal pretreatment

For hydrothermal pretreatment, around 15 kg of raw bagasse (50% w/w moisture content) were fed into a 350 L alloy steel reactor (Pope Scientific Inc., Saukville, USA), without previous milling or washing, with 9% (w/w) solids loading. No attempts were made in order to optimize the pretreatment operational parameters. The reaction was performed at 190 °C by thermal fluid percolation through the reactor's jacket, for 10 min at 150 rpm [28]. After the reaction, the reactor was water-cooled, depressurized and opened.

Pretreated material fractions were separated by a nutsche filter (Pope Scientific Inc., Saukville, USA) with 140 L capacity. The solid fraction, mainly composed of cellulignin, was stored in a refrigerated container to be later subjected to an enzymatic hydrolysis step (data not shown). The liquid fraction, HH, was concentrated three times in a wiped film evaporator (Pope Scientific Inc., Saukville, USA) with capacity up to 50 $kg \cdot h^{-1}$ of water evaporation and stored in a refrigerated container for the post-hydrolysis assays.

2.3. Acid post-hydrolysis

2.3.1. Experimental design

For three acids—sulfuric, oxalic and maleic—seven post-hydrolysis assays were performed following a 2^2 full factorial design with three central point repetitions. Temperature (120 °C, 135 °C and 150 °C) and acid loading (0.5%, 1.25% and 2.0% w/w) were considered as factors; xylose release and furfural production were considered as response variables. Reaction time ranged from 50 to 100 min, depending on the severity of the condition, and it was assessed in short time intervals to determine pentose (arabinose and xylose), acetic acid and furfural kinetic profiles. Sulfuric, oxalic, maleic acid and all other reagents and chemicals, unless otherwise noted, were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.3.2. Post-hydrolysis assays

Approximately 850 mL of the HH were fed into a 2 L alloy steel reactor (Parr Instrument Company, Moline, United States) and heated by electrical resistance until the reaction temperature was reached. Stirring was kept constant at 200 rpm. Sulfuric, maleic or oxalic acid (50 mL) were added by an external hydraulic pump over five minutes. After the addition, hemicellulosic post-hydrolysate (HPH) samples were periodically collected from the reactor through its dip tube. The reaction was stopped by cooling the reactor with cold water. The samples were analyzed by HPLC for sugars (xylose, arabinose, glucose and cellobiose), sugar degradation products (furfural, 5-hydroxymethylfurfural [HMF] and formic acid) and acetic acid content.