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Comparative material balances and preliminary technical analysis of the pilot scale sugarcane bagasse alkaline pretreatment to 2G ethanol production

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ABSTRACT

Material balance and preliminary technical analyses of pilot scale sugarcane bagasse alkaline pretreatment, using sodium hydroxide with and without anthraquinone (AQ) addition were analyzed and compared to elucidate the carbohydrates and phenolic components flux in the streams.

The lowest carbohydrates solubilization rates (9% wt for cellulose and 41% wt for hemicelluloses) were reached for the condition at 130 °C with AQ addition, however the highest lignin solubilization (87% wt) was accomplished for the condition using 170 °C with AQ addition. Preliminary technical analysis was carried out to evaluate the performance of the best pretreatment condition when integrated to a first and second generation ethanol plant, in a biorefinery concept, showing that 83.03 m^3/h of ethanol can be produced by this process. Ethanol production (in L/ton biomass) for proposed process is 8.1% lower than the expected for short terms technologies concluding that upgrades on the process, as higher solids concentrations and lignin energy use or, principally, lignin valorization must be performed to allow viability of the process.

1. Introduction

Energy and prosperity are related, so energy is indispensable for modern societies. Currently, about 85% of energy consumed worldwide is from non-renewable fossil sources as petroleum, natural gas and coal. The rampant use of petroleum products increases concerns about energy security, economic, and environmental issues. In this context, production and use of renewable energy resources assume a high priority to ensure global energy security (Pereira et al., 2015; Sun et al., 2015). Among the potential of renewable energy sources, lignocellulosic biomass has been identified as an important feedstock for the production of biofuels and other value-added products, thus contributing to the global energy supply (Chaturved and Verma, 2013). The second generation (2G) ethanol production from lignocellulosic biomass has been considered to be the biofuel with the greatest potential to replace oil-based fuels (Macrelli et al., 2012; Seabra et al., 2010).

Nguyen and Bowyer (2017) reported that production of second generation biofuels began at full commercial scale in 2015 and by that time, 67 s-generation biofuel facilities was operating around the world with one-third of these operating at commercial scale. DuPont opened, in 2015, the world's largest cellulosic ethanol plant (in Nevada, Iowa, processing corn stover with 30 million gallons of ethanol per year capacity) in contrast to what was happening when several large biofuel producers, including Abengoa, BP, and DuPont, closed plants or suspended projects. Currently, even DuPont ethanol plant in Nevada has shut down.

Though, even with some commercial lignocellulosic ethanol units operating, the production of second generation ethanol from biomass has not had their potential fully explored yet (Barakat et al., 2014; Dias et al., 2014).

A major bottleneck of the production is related to pretreatment step. Among the variety of pretreatments available, each one has a specific effect on biomass components, so different pretreatment methods and conditions should be chosen according to the process configuration selected for the subsequent hydrolysis and fermentation steps (Maurya et al., 2015). In this sense, a clear understanding of the chemical alterations that occur during biomass pretreatment is fundamental for

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process control and optimization considering that pretreatment is the most energy intensive and expensive step for the lignocellulosic production of ethanol (Ramirez et al., 2013; Wyman, 2007).

In an effective pretreatment, all the biomass components should be recovered in a way that they can be upgraded to valuable products, but important material losses often occur which affect the economic viability of the process. Since many pretreatment studies report only the compositional analysis of the streams, it is often difficult to verify the integrity of the biomass components. Mass balance calculations allow assessing the recovery of each component and the material losses occurring in each unit operation (Hatzis et al., 1996).

Pretreatment methods usually result in liquid and solid streams, with variations in the quantity and type of solubilized components, depending on the performed technology. An effective comparison and evaluation of the pretreatment flux should be based on a mass balance approach, in order to track all carbon-based compounds in all of the process streams (Garlock et al., 2011).

All processes comprised of more than one unit operation will have losses on intermediate streams. If the process yields are calculated based on the initial biomass composition without taking into account any pretreatment mass losses related to solid-liquid separation or post-washing, for example, the results will not be correct (Hatzis et al., 1996; Garlock et al., 2011).

The application of the law of conservation to analyze a process system by accounting for the mass of each reactant/product entering or leaving a process unit is extremely important for the design and optimization of bioconversion/biorefinery processes (Garlock et al., 2011; Burkhardt, 2010). In addition, tracking the destination of cellulose and hemicelluloses throughout the process makes it possible to effectively compare different pretreatments and to generate accurate yields (Garlock et al., 2011).

Close material balance is a difficult challenge due to the complexity of measuring all the carbon-based compounds, but is the most reliable way to compare and scale up the process (Schell et al., 2001). Based on this concept, the objective of this work is to evaluate the mass balance around the alkaline pretreatment of sugarcane bagasse in pilot scale, with and without anthraquinone (AQ) addition. The experimental data was also used to perform a preliminary technical analysis, considering the integration of the alkaline pretreatment on an integrated 1st and 2nd generation ethanol production process.

2. Materials and methods

2.1. Raw material

Fresh sugarcane bagasse was provided by the sugar and ethanol plant Pedra Agroindustrial located in Serrana, São Paulo, Brazil. The predominant cane variety was SP81-3250.

2.2. Pretreatment

Sodium hydroxide pretreatment (with and without anthraquinone (AQ) addition) was previously optimized in lab-scale by our work group using a 2^3 full factorial design, to evaluate the influence of the pretreatment operational conditions (time, temperature and NaOH loading) on the subsequent cellulose, hemicellulose and lignin solubilizations (Nascimento et al., 2016). Based on the results of this previous work, the best two conditions for the alkaline pretreatment were selected and performed, with and without AQ addition, in pilot scale. The operational conditions were identified as: PT130 (130 °C, 30 min, 1.5% w/v NaOH) and PT170 (170 °C, 30 min, 1.5% w/v NaOH), using suffix $_{AQ}$ when anthraquinone (0.15% (w/w)) was used in the reaction ($PT130_{AQ}$ and $PT170_{AQ}$).

The reactions were carried out in a 350 L capacity reactor, built of 276 hastelloy steel, designed by CTBE/Pope Scientific INC, equipped with a stirrer, and heated through a jacket with thermal oil or steam injection.

The reactor was loaded with 180 L of water and heated to 90 °C. After that, 12 kg of sugarcane bagasse (dry basis) and NaOH solution (for final concentration of 1.5% w/v) were added in the reactor, achieving a liquid-to-solid ratio of 15:1. Reactions were performed with or without addition of 0.15% (w/w) of anthraquinone (AQ).

The reaction mixture was heated to the assay temperature (130 °C and 170 °C), and held under stirring for the reaction time (30 min). When the reaction time had elapsed, the reactor was discharged, and the solid fraction (hereafter referred to as pretreated material) was separated from the lignin-rich soluble fraction (black liquor) by filtration in a Nutsche filter with 100 L capacity (Pope Scientific INC- 276 Hastelloy steel). Pretreated material were submitted to washing steps, using 50 L of water in each wash, in order to remove the soluble lignin, and adjust the pH near to neutral. The amounts of extracted components decreased with the number of washes, with very low concentrations after the third washing step.

The pretreated material was thoroughly washed in the Nutsche filter until pH 7 was reached. Lignin was recovered from the black liquor by acidification of medium as described in Section 2.3.

After pretreatment, the solid fraction was weighed to determine mass yield, submitted to chemical characterization (as described in Section 2.5) and stored at 4 °C for further applications. Reactions were performed in duplicate.

The pretreatment selectivity, ability to selectively remove lignin without extensive attack on carbohydrate fractions, is defined as the ratio of lignin removed to the amount of carbohydrates removed at a particular time during pretreatment (Ramirez, 2010).

2.3. Lignin precipitation and recovery

Lignin was isolated from the black liquor by precipitation after acidification. The black liquor and the two first wash waters were transferred to a 500 L stirred tank, and approximately 1.5 L of 98% sulfuric acid was added until a pH of approximately 2.0 was reached under mechanic agitation. Since the concentration of soluble lignin in the effluent of the third, fourth and fifth wash was negligible, just the first liquor (black liquor), 1st and 2nd wash streams were considered for further lignin recovery using sulfuric acid as precipitator agent. The precipitated lignin was separated by filtration in a filter press (Bomax/Prensamax400) and washed six times with water until a final pH of approximately 6.0 was achieved. The washed lignin was dried at room temperature, weighed and characterized as described in item 2.5.

2.4. Determination of monomeric and oligomeric sugars in the wash stream of lignin precipitation

Monomeric sugars and organic acids (formic and acetic acids) were analyzed using a HPLC system 1260 Infinity (Agilent, Santa Clara, USA) equipped with refractive index (RI) detector. The analytical Aminex HPX-87H column (300 mm × 7.8 mm, 5 µm) was used in combination with a guard column Micro-Guard Cation PC H Refill Cartridges (Bio-Rad Laboratories, Hercules, USA). The mobile phase was sulfuric acid (5 mmol L^{-1}) at flow rate of 0.6 mL min^{-1} at 35 °C. For the analysis of furfural and 5-hydroxymethylfurfural (HMF), a reversed-phase HPLC equipped with an Acclaim 120 C18 column (150 mm × 4.6 mm, 3 µm) and a single wavelength UV detector were used. The mobile phase was water-acetonitrile 1:8 (v/v) with 1% acetic acid (v/v) at a flow rate of 0.8 mL min^{-1} at 25 °C. Run time was 30 min.

Oligomeric sugar analysis was conducted using the standard NREL method for oligomeric sugar determination of liquid streams (Sluiter et al., 2008) which uses a post-hydrolysis with sulfuric acid 4% (w/w) at 121 °C for 1 h. The oligomeric sugar concentration was calculated as the difference between the monosaccharide content measured via HPLC before and after the acid hydrolysis.

Total phenolic compounds content, present in the washed water was