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Contributing to the environmental sustainability of the second generation ethanol production: Delignification of sugarcane bagasse with sodium hydroxide recycling

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ABSTRACT

A process able to perform the complete separation of the sugarcane bagasse components, making them useful for specific purposes with low water and reactant consumption is environmental and economically desirable. In this work we evaluated the pH influence on alkaline delignification of pretreated sugarcane bagasse by steam explosion, in a pilot plant, recycling the black liquor for cellulosic pulp obtainment, focused on second generation ethanol production. The black liquor was recycled four times with no pH adjustment (Series A) and for 11 times adjusting the pH (Series B). In Series A experiments lignin was not entirely removed after the third recycling reaction. NaOH can be recycled as black liquor but it is essential to maintain the pH in 13.3–12.6 range before each new delignification cycle (Series B). The reduction in water consumption can reach 65% considering the volume of black liquor produced by lignin amount recovered. The quality of the cellulosic pulp produced is not changed significantly after each reaction, making it suitable for second generation ethanol production. Preliminary calculations showed that 38% of the NaOH used can be saved, contributing to a better life cycle for this process.

1. Introduction

High fuel prices and concerns about climate change are boosting biofuels development. In this context lignocellulosic materials are interesting feedstocks for satisfying the increasing ethanol demands without affecting arable areas needed for production of food and feed (Hahn-Hagerdal et al., 2006).

However, the production of biomass and its conversion into value added products requires large amounts of water and reactants, which can create a large environmental impact (Balat, 2011; Singh and Kumar, 2011; Gerbens-Leenes et al., 2009). Reducing the water consumption during biomass cultivation and biofuels production have a crucial importance for the establishment of a strong biofuels market, especially for 2nd generation biofuels (Sims et al., 2010), where water and reactants such as sodium hydroxide are intensively used during biomass fractionation, for example, in the delignification process (Cardona et al., 2010). Technological improvements are necessary in alkaline delignification processing to improve the environmental sustainability of the future second generation ethanol production (Dias et al., 2012).

Brazil is the largest producer of sugar and ethanol from sugarcane in the world, generating large amounts of the fibrous residue sugarcane bagasse. In the 2012/2013 harvest, around 590 million tons of sugar cane was crushed and 23.2 million cubic meters of ethanol were produced (UNICA, 2012). In this context, lignocellulosic materials are interesting feedstocks for satisfying the increasing market of ethanol and biorenewable (Hahn-Hagerdal et al., 2006).

The fragmentation of sugarcane bagasse into cellulose, hemicellulose and lignin, could be used in more than forty different applications by biotechnological and non-biotechnological methods, such as: ethanol (Nigam and Singh, 2011), polymer films (Hartman et al., 2006), pulp and paper (Lima et al., 2003), enzymes,

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gradual release formulations of pesticides and fertilizers (Pereira et al., 2003), single cell proteins, chelating agents for heavy metals (Gonçalves and Luz, 2001; Quintana et al., 2008), butanol, animal feed, natural adhesives resins (Amaral-Labat et al., 2008), furfural, xylitol, carboxymethyl cellulose (Pushpamalar et al., 2006), nanocomposites (Orts et al., 2005) and other products following the biorefinery concept (Gálvez, 2000; Pandey et al., 2000; Mussatto et al., 2006; Cardona et al., 2010; Chandel et al., 2012).

In order to use integrally the biomass, firstly an effective reduction of the recalcitrance is required for the releasing of the locked polysaccharides in the lignin-carbohydrate complex. This is the basis for the emerging cellulosic-ethanol and related bio-based chemical industries (Wyman, 2007; Zhang et al., 2007). The disruption of the cellulose–hemicellulose–lignin association is usually achieved through a pretreatment reaction and/or delignification process which requires large amounts of water and chemicals (Kumar et al., 2009; Yang and Wyman, 2008).

Many authors have been trying to find the best conditions for separating the main constituents of lignocellulosic biomass as efficiently as possible, including pretreatments such as steam explosion (Martin et al., 2008; Rocha et al., 2012b; Kaar et al., 1998), acid hydrolysis (Gámez et al., 2006; Neureiter et al., 2007) and organosolv (Moriya et al., 2007; Mesa et al., 2010). The main goal of these pretreatments are usually to remove or modify the lignin and the hemicellulose structures to turn the cellulose into a substrate that is more accessible to enzymatic attack (Martin et al., 2008).

The enzymatic hydrolysis of the lignocellulosic material in its native state is very slow and not commercially feasible (Focher et al., 1990). The same problem is found for chemical processes, however the hemicellulose removed by a pretreatment process such as steam explosion followed by acid and enzymatic hydrolysis increases the diffusion and the selectivity of cellulose hydrolysis (Excoffier et al., 1990; Marchessault, 1990). Moreover the alkaline delignification step with subsequent enzymatic hydrolysis step leads to higher yields due to the lignin removal. Procedures performed in our laboratories for separation of sugarcane bagasse constituents in a two-step process showed that in the first step the hemicellulose fraction was isolated with high yield by steam explosion pretreatment performed at 190 °C, for 15 min. In the second step, lignin was extracted by alkaline delignification process performed at 100 °C for 1 h. Regarding lignin extraction, the efficiency of this process was 87% and the cellulose fraction was left unchanged, with 5% maximum residual lignin (Rocha et al., 2012b).

Although the yields improved, higher environmental impact in second generation ethanol scenarios are mainly related to high NaOH consumption for delignification prior to hydrolysis, being the most impacting parameter in Global Warming Potential (GWP) (Dias et al., 2012). According to this, technological improvements, such as NaOH recycling, are necessary in this process for the environmental sustainability of second generation ethanol production.

According to these criteria, the objective of this work was to evaluate the alkaline liquor recycling in the delignification step and also to obtain physical and chemical parameters for continuous pilot-scale process implementation.

2. Materials and methods

2.1. Substrate

Fresh sugarcane bagasse was provided by the Iracema sugar and ethanol mills, located in Iracemápolis, São Paulo, Brazil. The material was dried at room temperature and kept in a refrigerator under 4 °C until used.

2.2. Pretreatment

The raw sugarcane bagasse was submitted to steam explosion pretreatment under 190 °C and 15 min (Rocha et al., 2012a). The sugarcane bagasse samples pretreated by steam explosion, with low hemicelluloses content, are referred as cellulignins.

2.3. Delignification

The reactions were carried out in a 25-L stainless steel iron-carbon-coated reactor with agitation system and heating jacket (Fig. 1).

First, 15 L of water was heated at 98–100 °C. After that 1 kg (dry basis) of cellulignin and about 5 L of a aqueous solution containing 200 g of NaOH were added reaching a final concentration of NaOH 1% (w/v) and the solid/liquid ratio 1:20 (w/v). The reactor was closed and kept at 98–100 °C for 1 h, at 100 rpm (Rocha, 2000).

After delignification the reactor was unloaded and the mixture centrifuged at 1700 rpm producing the black liquor containing lignin and a solid fraction, (cellulosic pulp). The liquor was collected and the cellulosic pulp was washed with water until pH 6, both of them were stored at 4 °C for further characterizations.

The black liquor was further used as delignification solution in another reaction with new cellulignin, following the same experimental conditions described above, and the new liquor obtained was used again and successively more times. For the first series of experiments, the liquor was reused four times and no pH adjustment was performed between the reactions (Series A); for the second series, the liquor was reused 11 times, the pH was adjusted to 13 with NaOH before the reaction and the total alkali amount quantified (Series B).

2.4. Chemical analysis of bagasse, cellulignin and cellulosic pulp samples

Samples of the bagasse were milled to pass through a 0.75 mm screen. Approximately 2 g of milled sample was extracted with 95% ethanol for 6 h in a Soxhlet apparatus. Ash content was determined after burning of the samples in a muffle 600 °C for 4 h (ASTM E1755-01, 2003). Extracted bagasse samples were hydrolyzed with 72% sulfuric acid at 45 °C for 7 min. The acid was diluted to a final concentration of 3% (addition of 275 mL of water) and the mixture heated at 121 °C, 1 atm for 30 min. The residual material was cooled and filtered in a paper filter. The solids were dried to constant weight at 105 °C and determined as insoluble lignin (Gouveia et al., 2009). The soluble lignin concentration in the filtrate was determined by measuring absorbance at 280 nm (Rocha et al., 2012b) using Eq. (1).

$$C_{Lig} = 4.187 \times 10^{-2}(A_{Lig280} - A_{pd280}) - 3.279 \times 10^{-4} \quad (1)$$

where C_{Lig} is the concentration of lignin ($g\,L^{-1}$) A_{Lig280} is the absorbance at 280 nm of lignin solution; $A_{pd280} = c_1\varepsilon_1 + c_2\varepsilon_2$ is the Absorbance in 280 nm of sugar decomposition products (furfuraldehyde and HMF), whose concentrations c_1 and c_2 were determined through HPLC and ε_1 and ε_2 through UV spectroscopy (Rocha et al., 2012b).

The concentrations of monomeric sugars in the soluble fraction (hydrolyzate) were determined by HPLC using a BIORAD HPX87H column at 45 °C, eluted at the 0.6 mL min^{-1} with 0.005 mol L^{-1} sulfuric acid. Sugars were detected in a 30 °C temperature controlled RI detector (Knauer HPLC pump and detector). The factors used to convert sugar monomers to anhydromonomers were 0.90 for glucose and 0.88 for xylose and arabinose. Acetyl content was calculated as the acetic acid content multiplied by 0.72. These factors were calculated based on water addition to polysaccharides during