Production of bioethanol, methane and heat from sugarcane bagasse in a biorefinery concept

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A B S T R A C T

The potential of biogas production from the residues of second generation bioethanol production was investigated taking into consideration two types of pretreatment: lime or alkaline hydrogen peroxide. Bagasse was pretreated, enzymatically hydrolyzed and the wastes from pretreatment and hydrolysis were used to produce biogas. Results have shown that if pretreatment is carried out at a bagasse concentration of 4% DM, the highest global methane production is obtained with the peroxide pretreatment: 72.1 L methane/kg bagasse. The recovery of lignin from the peroxide pretreatment liquor was also the highest, 112.7 ± 0.01 g/kg of bagasse. Evaluation of four different biofuel production scenarios has shown that 63–65% of the energy that would be produced by bagasse incineration can be recovered by combining ethanol production with the combustion of lignin and hydrolysis residues, along with the anaerobic digestion of pretreatment liquors, while only 32–33% of the energy is recovered by bioethanol production alone.

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1. Introduction

In recent years, efforts have increased toward the commercial production of ethanol, considered the most promising biofuel from renewable resources. The development of second generation bioethanol made from lignocellulosic biomass can increase the sustainability of feedstock production without competing with food production or the cultivation of farmland. Unfortunately, this process is very costly in terms of the energy input required. However, the possibility of using the lignocellulosic material in its entirety, thus linking bioethanol production with the coproduction of thermochemical fuels and/or power, can reduce production costs by minimizing the utilization of fossil energy sources and reusing the excess material and by-products of the technology employed (Laser et al., 2009).

Among the various agricultural crop residues, sugarcane bagasse is the most abundant lignocellulosic material in tropical countries. In Brazil, as a general rule, 1 ton of sugarcane generates 280 kg of bagasse and the estimate for the 2011/2012 sugarcane harvest is of 568.50 million tons (UNICA, 2011). About 50% of this residue is used in distillery plants as a source of energy; the remainder is stockpiled (UNICA, 2011). Due to the amount of this biomass as an industrial waste, there is great interest in developing in a biorefinery concept, methods for the production of fuels and chemicals that offer economic, environmental, and strategic advantages.

A biorefinery integrates biomass conversion processes to produce fuels, electrical power and chemicals from biomass and, as such, is analogous to a petroleum refinery (Cherubini, 2010). By producing multiple products, a biorefinery can take advantage of the differences in biomass constituents and intermediates and maximize the value derived from the biomass feedstock according to the market situation and biomass availability (Luo et al., 2011). Bagasse, like all lignocellulosic materials, has three major constituents: cellulose, hemicellulose and lignin which, due to its recalcitrant nature, cannot be easily separated into readily utilisable components. Thus, second generation bioethanol production involves four steps: pretreatment, to render the cellulose accessible; hydrolysis with the addition of enzymes or an acid catalyst to release the monomeric sugars; fermentation to convert sugars into ethanol; and finally, distillation for product recovery (Margeot et al., 2009).

Pretreatment is one of the most expensive and least technologically-mature steps in the process of converting biomass to fermentable sugars. Hence, it offers a great potential for improvement in efficiency and the reduction of costs through research and development (Mosier et al., 2005). In this work, two promising pretreatment technologies were used: pretreatment with lime...
(Fuentes et al., 2011; Rabelo et al., 2008) and pretreatment with alkaline hydrogen peroxide (Rabelo et al., 2008; Rivera et al., 2010). They were chosen because they can be carried out in conditions of moderate temperature and pressure and without acids.

Lime pretreatment has low formation of fermentation inhibitors, increases pH and provides a low-cost alternative for lignin solubilization, removing approximately 33% of lignin and 100% of acetyl groups. The action of lime is slower than that of other pretreatment chemicals but its low cost and safe handling makes it attractive (Wyman et al., 2005).

Furthermore, lime can be easily recovered as calcium carbonate by neutralization with carbon dioxide, although this is an energy-intensive process and as yet, is not economically feasible. The calcium hydroxide can be subsequently regenerated using established kiln technology (Kaar and Holtzapple, 2000).

Hydrogen peroxide is a well-known reagent in the paper and cellulose industry, where it is used as a bleaching agent. It also has the great advantage of not leaving residues in the biomass as it degrades into oxygen and water. Furthermore, the formation of secondary products is practically nonexistent. This agent has been shown to be an excellent choice for the pretreatment of sugarcane bagasse, leading to almost 100% recovery of the cellulose as glucose after enzymatic hydrolysis (Rivera et al., 2010).

Biomass ethanol production generates great amounts of residuals, both liquid and solid. Among the liquid residuals are the pretreatment liquor, rich in pentoses, soluble and insoluble lignin; and the vinasse, the effluent after ethanol recovery. There are also solid wastes from the hydrolysis process, composed mainly of lignin and hemicelluloses that are not solubilized during pretreatment and hydrolysis.

One of the great challenges of ethanol production from biomass is the use of all wastes left over from the process. It is probably only in this way that the process can be made economically viable as well as environmentally sustainable. The best use for the pentoses in the pretreatment liquor is ethanol production; however, current processes using existing microorganisms lead to extremely low yields (Kaparaju et al., 2009). The development of genetically-modified microorganisms that can convert pentoses into ethanol is being assessed by different research groups but no viable industrial process has been developed up to now. There exist some methods for vinasse re-use, such as thermal concentration, land application, for cattle feed, fungi production and recycling of vinasse into partially dilute molasses in fermentation (Andrade et al., 2009).

Another alternative for the use of these wastes is biogas production, which can be a sustainable solution for the organic matter removal from effluents. Another further advantage here is the possibility of using the new effluent resulting from biogas production as fertilizer on agricultural soils (Liu et al., 2006). Before using the residual liquid, lignin can be precipitated and used for heat and energy production (Sassner et al., 2008), though this requires additional energy input to reduce the water content. In the current study, several scenarios for bioethanol production and co-production of electrical power and biogas using dry bagasse as substrate were investigated and compared in terms of gross energy output. Ethanol was produced from bagasse pretreated with either lime or hydrogen peroxide-pretreated bagasse, using sequential hydrolysis and fermentation (SHF). Methane and power were produced from the process residues of ethanol production. The primary aim was to compare the energy output per unit of bagasse mass for the different scenarios (1) Combustion of untreated bagasse, (2) bioethanol from pretreated bagasse, (3) bioethanol from pretreated bagasse, lignin combustion, and biogas from pretreatment liquor and hydrolysis residue, (4) bioethanol from pretreated bagasse, lignin and hydrolysis residue combustion, biogas from liquor pretreatment.

### 2. Methods

#### 2.1. Process description

Based on the above considerations, the bagasse biorefinery concept was developed to produce biofuel (bioethanol) and the process effluents were characterized and utilized for the production of additional biofuel (methane) and power (lignin and/or enzymatic hydrolysis residue) to improve the overall recovery of bioenergy from sugarcane. The scheme of the integrated process adopted in this paper can be seen in Fig. 1.

#### 2.2. Raw material

Sugarcane bagasse (Saccharum officinarum) from a single harvest was obtained from the Usina São Luiz-Dedini S/A sugar plant (Pirassununga/SP, Brazil). It was dried at 45 °C for 48 h, left for 48 h at room temperature, put into plastic bags and kept in a storage room. The dry matter content (DM) was approximately 95%.

#### 2.3. Pretreatment methods

The pretreatments were carried out in optimal conditions as determined in previous studies (Fuentes et al., 2011; Rabelo et al., 2008; Rivera et al., 2010). Biomass concentrations in each pretreatment were varied to determine the maximum solids concentration compatible with good performance.

##### 2.3.1. Calcium hydroxide (lime) pretreatment

The studies were done with solids concentrations of 4%, 5%, 6%, 7% and 8% DM. The material was treated with a lime solution prepared by dissolving 0.47 g/g DM in 100.0 mL distilled water. In all the assays, a certain amount of lime remained insoluble although it continued to dissolve during pretreatment. The flasks were incubated in an orbital shaker MA-832 (Marconi, Piracicaba, SP, Brazil), agitated at 150 rpm, 90 °C for 90 h (Fuentes et al., 2011; Rabelo et al., 2008).

##### 2.3.2. Alkaline hydrogen peroxide pretreatment (AHP)

The pretreatment was performed with solids concentrations of 4%, 5%, 6%, 7% and 8% DM. A hydrogen peroxide solution was prepared by dissolving 7.36% (v/v) of H2O2 in 100.0 mL distilled water and adjusting the pH to 11.5 with sodium hydroxide. The flasks were incubated in an orbital shaker MA-832 (Marconi et al., 2008; Rabelo et al., 2008) and pretreated in an orbital shaker MA-832 (Marconi, Piracicaba, SP, Brazil), agitated at 150 rpm, 90 °C for 90 h (Fuentes et al., 2011; Rabelo et al., 2008).

#### 2.3.3. Bioethanol production

The pretreatment was performed with solids concentrations of 4%, 5%, 6%, 7% and 8% DM. A hydrogen peroxide solution was prepared by dissolving 7.36% (v/v) of H2O2 in 100.0 mL distilled water and adjusting the pH to 11.5 with sodium hydroxide. The flasks were incubated in an orbital shaker MA-832 (Marconi et al., 2008; Rabelo et al., 2008) and pretreated in an orbital shaker MA-832 (Marconi, Piracicaba, SP, Brazil), agitated at 150 rpm, 90 °C for 90 h (Fuentes et al., 2011; Rabelo et al., 2008).

#### 2.4. Fermentation

Fermentation was assessed in an orbital shaker MA-832 (Marconi, Piracicaba, SP, Brazil), agitated at 150 rpm, 90 °C for 90 h (Fuentes et al., 2011; Rabelo et al., 2008).
con, Piracicaba, SP, Brazil), agitated at 150 rpm, at 25 °C for 1 h (Rabelo et al., 2008; Rivera et al., 2010).

2.4. Pretreatment liquor and precipitated lignin

After the pretreatment step, the liquors were separated from the solid fraction by filtration and then reserved for the precipitation of lignin.

The solids fraction was washed several times for removal of the water-soluble solids (WS) and used to determine the solids recovery yield and chemical composition (Sluiter et al., 2008a,b).

The insoluble lignin was precipitated using a 1% (v/v) solution of hydrochloric acid down to pH 2 (Ibrahim and Chuah, 2004) and the liquor was centrifuged at 3000 rpm to obtain the liquid fraction (soluble sugars) that was used for biogas production.

2.5. Enzymatic hydrolysis

The enzymatic hydrolysis of the washed material was performed using a substrate concentration of 3.0% (w/w) WIS (water-insoluble solids) in flasks incubated in an orbital shaker MA-832 (Marconi, Piracicaba, SP, Brazil) agitated at 100 rpm at 50 °C. The pH was adjusted to 4.8 with 0.05 mol/L sodium citrate buffer.

Cellulose from T. reesi (Sigma–Aldrich Corporation, St. Louis, MO, USA) was added at a concentration corresponding to 50 FPU/g WIS for the material pretreated with lime and 3.5 FPU/g WIS for material pretreated with hydrogen peroxide. β-glucosidase from Aspergillus niger (Sigma–Aldrich Corporation, St. Louis, MO, USA) was added at a concentration corresponding to 25 UI/g WIS for both pretreated materials.

Cellulase activity was determined as filter paper units per milliliter, as recommended by the International Union of Pure and Applied Chemistry (Ghose, 1987). β-glucosidase activity was determined through a solution of cellobiose 15 mmol/L and expressed in units per milliliter (IU/mL) (Wood and Bhat, 1988). Enzyme activity was 47.44 FPU/mL for cellulases and 343.63 IU/mL for β-glucosidase.

After enzymatic hydrolysis, the liquid fraction rich in glucose was used for ethanol production by fermentation of the liquor by Saccharomyces cerevisiae was used for ethanol production by fermentation of the liquor by T. reesei. Cellulase from T. reesei (Sigma–Aldrich Corporation, St. Louis, MO, USA) was added at a concentration corresponding to 50 FPU/g WIS for cellulases and 343.63 IU/mL for β-glucosidase.

After enzymatic hydrolysis, the liquid fraction rich in glucose was used for ethanol production by fermentation of the liquor by T. reesei. Cellulase from T. reesei (Sigma–Aldrich Corporation, St. Louis, MO, USA) was added at a concentration corresponding to 50 FPU/g WIS for cellulases and 343.63 IU/mL for β-glucosidase.

2.6. Analytical methods

2.6.1. Solid fraction after pretreatment (bioethanol production)

Extractives, structural carbohydrates and lignin were analyzed in accordance with Sluiter et al. (2008a,b). Prior to compositional analysis the samples were finely ground in a knife mill MA-630/1/E (Marconi, Piracicaba, SP, Brazil).

Sugars and organic acids, HMF and furfural were analyzed with an HPLC system (Waters Corporation, Milford, MA, USA) equipped with a refractive index detector. Cellulbiose, glucose, xylose, arabinose and mannose were separated on a Sugar-Pak I column (Waters Corporation, Milford, MA, USA) run at a flow rate of 0.5 mL/min at 70 °C, with water as the eluent. Acetic acid, HMF, furfural, lactic acid, formic acid and levulinic acid were separated using an Aminex HPX-87H column (Bio-Rad Laboratories Inc., Hercules, CA, USA) at 65 °C with 0.5 mL/min of H2SO4 at 5 mM as the eluent.

2.6.2. Pretreatment liquors and solids residues (methane production)

2.6.2.1. Chemical Oxygen Demand (COD). COD was determined using Spectroquant® test kits (Merck, Darmstadt, Germany) based on the oxidation of the sample through a heated sulfuric acid solution of potassium dichromate, using silver sulfate as the catalyst. Samples were analyzed in triplicate by adding 2.0 mL of diluted pretreatment liquor to tubes containing the oxidant solution and heated for 2 h at 150 °C. Thereafter, the tubes were cooled to ambient temperature and the solution was analyzed in a spectrophotometer HACH DR/2000 (Hach Company, Loveland, CO, USA) at 620 nm. The results obtained have been expressed in mg O2/L.

For the solid fraction, the COD was determined, as previously described, by adding 0.2 g of hydrolysis residue in the Spectroquant® test kits (Merck, Darmstadt, Germany).

2.6.2.2. Sugar concentration. The pretreatment liquor was analyzed by an HPLC equipped with a refractive index detector, in accordance with the National Renewable Energy Laboratory (NREL) standard procedure (Sluiter et al., 2008b). Approximately 5.0 mL of liquor was subjected to acid hydrolysis after the addition of sulfuric acid to a pH level of 2. The solution was hydrolyzed at 121 °C for 1 h. This step was necessary to ensure that all the oligosaccharides present were hydrolyzed to monosaccharides and could thus be quantified.

The separation was performed in a Sugar-Pak I column (Waters Corporation, Milford, MA, USA) at 70 °C with a flow rate of 0.5 mL/min, using filtered deionized water as the mobile phase.

2.6.2.3. Chemical composition. The chemical composition of the residues resulting from the hydrolysis was determined by the Van Soest method (Van Soest, 1963). The bagasse residue after enzymatic hydrolysis was analyzed by the FiberBag system (Gerhardt Analytical Systems, Königswinter, Germany). This involves a sequential extraction under neutral and acid detergent, followed by strong acid extraction. The different fractions were: (i) soluble in neutral detergent fraction (SND); (ii) hemicellulose (HEMI), which was extracted by acid detergent; (iii) cellulose (CELL), which was extracted by 76% sulfuric acid; (iv) lignin (LIGN).

2.6.2.4. Total solids (TS), dry matter (DM) and volatile solids (VS). Total solids (TS) or dry matter (DM) and volatile solids (VS) were determined in accordance with the Standard Methods (APHA, 1995). To determine TS or DM, approximately 20.0 mL of liquor or 2.00 g of hydrolysis residue were dried at 105 °C to constant weight. After this, to quantitate VS, the material was burnt in an oven at 550 °C for two hours.

2.6.3. Lignin characterization

Lignin samples obtained by the two pretreatments were analyzed for moisture content in accordance with the NREL standard procedure (Sluiter et al., 2008a). Samples of lignin were also analyzed by Differential Scanning Calorimetry (DSC) (Mettler-Toledo, Columbus, OH, USA) and had their molar weight distribution determined by Gel Permeation Chromatography (GPC) using a CLASS-LC10 data analyzer and a series of 500, 103 and 104 Å PLGel columns (Shimadzu, Kyoto, Japan).

2.7. Biomethane potential (BMP) tests

Methane production was assessed by batch biochemical methane potential (BMP) in mesophilic conditions (35 °C) in 100 mL reactors, samples of the pretreatment liquor and solid residues from hydrolysis were added to a solution of macroelements (sources of N, P, Mg, Ca, K), a solution of oligoelements, a solution of bicarbonate (buffer solution) and the inoculum (sludge from an anaerobic digester at a sugar factory, Marseille, France; its compo-
sition was 91.3 ± 0.002 g TS/L and 76.6 ± 0.001 g VS/L. The samples were added to obtain a concentration of 0.5 g COD/g TS of sludge. Once the reactors had been prepared, a depaerification with nitrogen was carried out to obtain anaerobic conditions.

Biogas production without the addition of liquor or hydrolysis residue was also carried out in order to quantify endogenous production and served as a negative control. In addition, biogas production with the addition of ethanol, a completely degradable material replacing pretreatment liquor or hydrolysis residue, was used as a positive control. BMP tests were duplicated and lasted up to 40 days. Liquor biodegradability was calculated on the basis of a theoretic production yield of 350 mL CH4/g COD (Angelidaki and Sanders, 2004).

2.8. Volume and composition of the produced biogas

Biogas volume was measured by vertical displacement of water in a gasometer and its composition was measured by a gas chromatograph Varian GC-CP4900 (Agilent Technologies, Santa Clara, CO, USA) equipped with two columns. The first one, a Molsieve 5A PLOT (Sigma–Aldrich Corporation, St. Louis, MO, USA), was used to separate O2, N2 and CH4 and the second, a HayeSep A column (Vici Valco Instruments Co. Inc., Houston, TX, USA), to separate CO2 from other gases. The detection of gaseous compounds was done using a thermal conductivity detector with an injected volume of 1.0 mL. Calibration was performed with a standard gas composed of 25.00% of CO2, 1.98% of O2, 10.00% of N2 and 63.02% of CH4.

3. Results and discussion

3.1. Chemical composition of solids fraction

Fig. 2 depicts the chemical composition of untreated bagasse, the solid fraction after pretreatment (4% DM) and solid residues after hydrolysis with the two catalysts.

One ton of bagasse (95% DM) gave a yield of 560.5 kg DM after lime pretreatment. Much of the cellulose was preserved in the solid fraction, representing 66.2% of pretreated material. Part of the hemicelluloses were solubilized, and this constituent represented 20.4% of the chemical composition of pretreated material. For bagasse pretreated with alkaline hydrogen peroxide, a yield of 433.2 kg DM was obtained, while the pretreated material was composed primarily of cellulose which represented 80.8% of the material. Much of the hemicelluloses was solubilized during pretreatment such that after pretreatment this constituent represented only 11.7% of the solid fraction. It can be seen from Fig. 2 that the residue from the hydrolysis of lime-pretreated bagasse had more hemicellulose, since this pretreatment solubilizes only a small part of this polymer. Although peroxide pretreatment is more efficient in solubilizing hemicelluloses, 40% of the residue after hydrolysis was hemicellulose, highlighting that it would be advantageous to use the residue for biogas production. There was almost no cellulose left in the residues; its amount was a little higher in the residue from lime-pretreated bagasse while the lignin composition was similar for the two residues.

3.2. COD analysis and sugar concentration

Results of COD in the samples of pretreatment liquor and hydrolysis residues are presented in Table 1. In addition, the table shows sugar concentration in the pretreatment liquor.

In Brazil, vinasse, obtained after distillation, presents a COD concentration of 1.0 g/L of hydrogen peroxide were higher than those for the pretreatment with lime. Besides the higher concentration of sugars in the liquor, which led to higher values of COD, the excess of hydrogen peroxide in the reaction medium could have further increased this value. Indeed, the residual concentration of hydrogen peroxide modifies the COD value by consuming the oxidizing agent potassium dichromate (K2Cr2O7), as shown in Eq. (1) (Talinli and Anderson, 1992).

\[ \text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{O}_2 + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{O}_2 + 7\text{H}_2\text{O} \] (1)

This interference can be corrected by knowing the residual concentration of hydrogen peroxide in each pretreatment liquor. According to Lin and Lo (1997), a concentration of 1.0 g/L of hydrogen peroxide is equivalent to 270 mg/L of COD. Similar results were obtained by Dantas (2005), who recorded 263 mg/L of COD in 1.0 g/L of hydrogen peroxide. Thus, even though there was residual peroxide in the pretreatment liquor, interference in the final COD was very low in comparison with the values given in Table 1.

It can also be noted from Table 1 that higher sugar concentrations were observed for liquors from alkaline peroxide pretreatment as this pretreatment solubilizes more hemicelluloses than the pretreatment with lime (Rabelo et al., 2008).

3.3. Volume and composition of the biogas produced

In this study, biomethane potential tests were carried out to estimate the potential production of biogas from the liquors from pretreatment and from the solid residues of hydrolysis. Methane

Table 1

<table>
<thead>
<tr>
<th>Concentration of solids in pretreatment (% DM)</th>
<th>COD (g O2/L or g O2/g biomass*)</th>
<th>Sugar concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lime</td>
<td>AHP</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>4</td>
<td>10.0 ± 0.1</td>
<td>21.4 ± 0.4</td>
</tr>
<tr>
<td>5</td>
<td>12.6 ± 0.0</td>
<td>23.2 ± 0.0</td>
</tr>
<tr>
<td>6</td>
<td>11.6 ± 0.3</td>
<td>27.7 ± 0.4</td>
</tr>
<tr>
<td>7</td>
<td>16.8 ± 0.9</td>
<td>37.0 ± 0.4</td>
</tr>
<tr>
<td>8</td>
<td>21.2 ± 0.1</td>
<td>43.5 ± 0.4</td>
</tr>
<tr>
<td>9</td>
<td>–</td>
<td>45.2 ± 0.7</td>
</tr>
<tr>
<td>10</td>
<td>–</td>
<td>58.2 ± 0.3</td>
</tr>
<tr>
<td>15</td>
<td>–</td>
<td>67.4 ± 0.9</td>
</tr>
<tr>
<td>4*</td>
<td>1.1 ± 0.0</td>
<td>1.1 ± 0.0</td>
</tr>
</tbody>
</table>

* Solid residues from hydrolysis.
potential can be expressed specifically per amount of waste (L CH₄/kg waste), per volume of waste (L CH₄/L-waste), per mass of volatile solids added (L CH₄/kg-VS) or per COD added (L CH₄/kg-COD). The volume is usually expressed in standard pressure (1 atm) and temperature (0°C) conditions (STP conditions) (Angelidaki and Sanders, 2004). In this work, the theoretic methane yields were based on the COD. To calculate the biodegradability, the theoretic methane production (350.0 NL/kg of COD) was considered.

Table 2 shows the composition of biogas and the methane yield (NL/kg of COD). The highest methane yield was obtained by working with 4% DM solids for both types of pretreatment. Considering the solid residue (residue after enzymatic hydrolysis), 162 ± 2 L/kg COD were produced for the hydrolysis residue of bagasse pretreated with lime in comparison to 152 ± 1 L/g COD for the hydrolysis residue of bagasse pretreated with hydrogen peroxide.

Fig. 3 shows the amount of methane produced per liter of pretreatment liquor, considering pretreatments performed with different solids concentrations (4–15% DM) and the amount of methane produced per ton of hydrolysis residue for the two types of pretreatment considered.

It can be noted from Fig. 3 that, in general, higher solids concentrations in the pretreatment step lead to larger volumes of methane produced, as higher solids concentrations produce higher concentrations of sugars and volatile acids in the reaction medium (not shown).

The highest production of methane was observed for the pretreatments with the highest solids concentration: 15% DM (peroxide pretreatment) and 8% DM (lime pretreatment). 6.5 ± 0.3 NL of methane/L pretreatment liquor were produced using the liquor from the pretreatment with peroxide and 3.13 ± 0.06 NL of methane/L pretreatment liquor using the liquor from the pretreatment with lime.

Fig. 3 also gives the volume of methane produced relative to the mass of hydrolysis residue put into the reactor for each pretreatment. It can be seen that the results are similar for both pretreatments: 167 ± 1 NL of methane/kg of residue was obtained with the residue of hydrolysis of bagasse pretreated with lime and 166 ± 2 NL of methane/kg of when the pretreatment was done with alkaline hydrogen peroxide.

In this work, experiments to determine the potential of biogas production from vinasse were not carried out, although the process stream could be diverted to biogas production. When pretreatment with alkaline hydrogen peroxide carried out with 4% DM is considered, 1 kg bagasse resulted in 25 L of pretreatment liquor and 0.0275 kg of hydrolysis residue. As 165.6 L of methane were produced per kg of hydrolysis residues and 2.7 L biogas were produced per liter of pretreatment liquor, it is possible to calculate a volume of 4.5 L of methane/kg bagasse from the hydrolysis residue and 67.5 L of methane/kg bagasse from the pretreatment liquor. Thus, the total biogas production was 72.1 L/methane/kg bagasse.

When the pretreatment was with lime (4% DM) 1 kg of bagasse resulted in the same volume of pretreatment liquor but 0.08225 kg of hydrolysis residue and 2.7 L methane were produced per kg of hydrolysis residue.

Table 2: Biogas composition and methane yield from anaerobic digestion.

<table>
<thead>
<tr>
<th>Concentration of solids in pretreatment (% DM)</th>
<th>Biogas composition (%)</th>
<th>CH₄ yield (NL CH₄/kg COD)</th>
<th>Biodegradabilityb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime</td>
<td>CO₂</td>
<td>CH₄</td>
<td>AHP</td>
</tr>
<tr>
<td>4</td>
<td>33.7 ± 1.4</td>
<td>66.3 ± 0.4</td>
<td>30.3 ± 1.1</td>
</tr>
<tr>
<td>5</td>
<td>31.1 ± 0.0</td>
<td>68.9 ± 0.2</td>
<td>33.2 ± 0.2</td>
</tr>
<tr>
<td>6</td>
<td>31.4 ± 0.3</td>
<td>68.6 ± 0.2</td>
<td>35.6 ± 0.2</td>
</tr>
<tr>
<td>7</td>
<td>29.8 ± 0.5</td>
<td>70.2 ± 0.6</td>
<td>34.9 ± 0.6</td>
</tr>
<tr>
<td>8</td>
<td>31.0 ± 0.3</td>
<td>69.0 ± 0.5</td>
<td>39.7 ± 0.4</td>
</tr>
<tr>
<td>9</td>
<td>31.4 ± 0.3</td>
<td>68.6 ± 0.2</td>
<td>35.6 ± 0.2</td>
</tr>
<tr>
<td>10</td>
<td>33.2 ± 0.4</td>
<td>67.1 ± 1.4</td>
<td>32.9 ± 0.4</td>
</tr>
<tr>
<td>15</td>
<td>33.9 ± 0.1</td>
<td>66.1 ± 0.2</td>
<td>33.9 ± 0.1</td>
</tr>
</tbody>
</table>

a Solid residues from hydrolysis.

b The ratio of measured CH₄ yield/theoretic CH₄ yield.
resulted in a production of 13.7 L of methane/kg bagasse from the hydrolysis residue and 45.0 L of methane/kg bagasse from the pretreatment liquor, making a total methane production of 58.7 L of methane/kg bagasse.

Lu et al. (2009), assessing the co-production of hydrogen and methane from cornstalks pretreated by steam explosion, obtained 63.7 and 114.6 L of hydrogen and biogas per kg of biomass, respectively. Bauer et al. (2009) evaluated a process for ethanol and methane production from steam-pretreated wheat straw. They proposed optimizing the second generation ethanol production process by using vinasse after ethanol production to produce biogas. They obtained 183 L of methane/kg of wheat straw from the vinasse. Kaparaju et al. (2009) evaluated the production of bioethanol, biohydrogen and biogas from hydrothermally-pretreated wheat straw. Pretreated biomass was enzymatically hydrolyzed and fermented to ethanol and biohydrogen. The effluents from the two processes were further used to produce methane with yields of 324 and 381 L/kg of volatile solids, respectively.

3.4. Lignin characterization

The lignin mass precipitated and its moisture content are given in Table 3 for both types of pretreatment studied. Moisture content directly influences the calorific value of a compound. Table 3 also shows the values of molecular weight average $M_w$ and number average $M_n$ molecular weights for the lignin obtained by precipitation of the pretreatment liquors from both reagents used. Polydispersity was calculated according to Eq. (2):

$$\text{Polydispersity} = \frac{M_w}{M_n}$$

From Table 3 it can be seen that lignin isolated from peroxide pretreatment liquor presented fragments with higher weight average molecular weights $M_w$ and had more fragments with different molecular weights, which is evidenced by the higher polydispersity.

Fig. 4 shows the curves of differential scanning calorimetry for samples of lignin precipitated from both pretreatment liquors. The exotherm of degradation of the lignin from lime pretreatment occurred around 413.5 °C with enthalpy of 67.9 J/g and the exotherm for the lignin from the peroxide pretreatment occurred at 400.6 °C and enthalpy of 52.5 J/g.

3.5. Mass balance and energy output

The mass flows for the two biorefinery alternatives are presented in Fig. 5 for both the lime (A) and alkaline hydrogen peroxide (B) pretreatments. Mass balance was expressed in terms of dry matter (DM) and the mass loss during chemical pretreatment of the biomass was considered in the calculation.

After pretreatment of one ton of bagasse with hydrogen peroxide, 45.6% DM remained in the solid fraction and the remaining 54.4% were extracted as hydrolysate. For lime pretreatment, 59.0% of DM remained in the solid fraction and 41.0% were extracted as hydrolysate.

For biomass pretreated with peroxide and lime, Fig. 6 introduces four possible scenarios proposed for optimizing bagasse use as well as the different contributions of individual biofuels in each scenario. It should be noted that the present study was carried out with the aim of comparing two pretreatment methods. It is a simplified analysis in which the energy requirements involved in biofuel production processes such as farming, harvesting, transporting, feedstock processing, fermentation, alcohol recovery, alcohol purification, biogas process, etc. were not considered. However, the energy requirements of these unit operations can be assumed to be the same whatever the pretreatment used.

The combustion of the 1 ton of bagasse (DM) produced 15,130.6 MJ of useful energy and was considered as the reference scenario (Scenario 1) (Dias et al., in press).

Among the scenarios studied (2, 3 and 4), the highest energy output for both types of pretreatments was obtained with scenario 4. The total energy output for this scenario was 10,731.2 MJ/ton bagasse and 10,281.7 MJ/ton bagasse when the pretreatment was with respectively alkaline hydrogen peroxide and lime.

In scenario 4, the hydrolyzed cellulose was used for bioethanol production leading to an energy generation of 5389.3 MJ/ton bagasse when bagasse was pretreated with peroxide and 5278.4 MJ/ton bagasse for pretreatment with lime. Ethanol production represented around 32% of the energy that can be produced from bagasse combustion and 50–51% of the total energy recovered in scenario 4. Part of the lignin was precipitated from the pretreatment liquor and used together with the hydrolysis residue of each pretreatment process for energy generation through direct combustion in boilers. The energy provided by burning the lignin was obtained through the mass of lignin recovered in each pretreatment, taking into account the calorific value of the lignin of 23.689 MJ/kg (Baker, 1983). By burning lignin, it was possible to obtain an energy output of 2895.9 MJ/ton bagasse for the lignin obtained from the pretreatment liquor from peroxide-pretreated bagasse and 2633.4 MJ/ton bagasse when pretreatment was with lime.

This energy from lignin represented 16–18% of the energy that can be produced from bagasse combustion and 26–27% of the energy recovered in scenario 4. Burning of the hydrolysis residue led to a generation of energy of 572.5 MJ/ton bagasse for peroxide pretreatment and 1458.5 MJ/ton bagasse for pretreatment with lime. Energy from burning hydrolysis residues represented 4–9% of energy that can be produced from bagasse combustion and 5–14% of energy recovered in scenario 4. Finally, the soluble fraction of the pretreatment liquor was used for biogas production, generating 1873.5 MJ/ton bagasse and 911.4 MJ/ton bagasse of energy for the liquor of bagasse pretreated with peroxide and lime, respectively.

### Table 3

Lignin characterization.

<table>
<thead>
<tr>
<th>Lignin</th>
<th>Lignin recovered (g/kg of bagasse)</th>
<th>Moisture content (%)</th>
<th>Weight average $M_w$</th>
<th>Number average $M_n$</th>
<th>Polydispersity $\frac{M_w}{M_n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime</td>
<td>139.63 ± 0.01</td>
<td>22.72 ± 0.5</td>
<td>907</td>
<td>460</td>
<td>3.66</td>
</tr>
<tr>
<td>AHP</td>
<td>147.28 ± 0.01</td>
<td>19.43 ± 0.1</td>
<td>952</td>
<td>502</td>
<td>3.88</td>
</tr>
</tbody>
</table>

Fig. 4. DSC profile representative of lignin degradation.
This energy represented 6–11% of the overall potential from bagasse combustion and 9–18% of energy recovered in scenario 4. Kaparaju et al. (2009), studying the hydrothermal pretreatment of wheat straw, obtained their best result for energy generation, on the basis of multiple biofuels, of 9364 MJ/ton wheat straw during the production of biogas, bioethanol and hydrogen. The authors also showed that when using biomass to produce only bioethanol, the energy output was 3572 MJ/ton wheat straw.

Using steam-pretreated hemp as the substrate, Kreuger et al. (2011) studied the co-production of ethanol and methane, obtaining a high yield: 11,100–11,700 MJ/ton processed dry matter which was more than twice the energy recovered by ethanol produced alone from hexoses: 4400–5100 MJ/ton processed.

Comparing scenarios 3 and 4, there is a decrease in the energy production of 3.93% and 11.22%, respectively when using bagasse pretreated with peroxide and lime, in scenario 3, the residue of enzymatic hydrolysis was directed to the production of biogas, which generated less energy than the straightforward burning of this residue. It is thus more advantageous to burn hydrolysis residues rather than to use them to produce biogas. Production of bioethanol alone (scenario 2) was of course the least energy-efficient process.
This study has not considered using vinasse for biogas production. According to Salomon and Lora (2009), for each liter of first generation bioethanol obtained after distillation, approximately 13 L of vinasse are produced and this is, in fact, the amount usually found in large-scale production plants in Brazil. This effluent is highly polluting but as high fertilizing value due to being rich in organic matter and having high BOD (Biological Oxygen Demand). The chemical composition of vinasse depends on the characteristics of the soil, the variety of sugarcane, the period of the harvest and the industrial process used for the production of ethanol.

According to Lettinga and Haandel (1993), 1 L of vinasse yields about 14.23 L of methane, which could represent a significant increase in useful energy production. Along with the methane produced by the anaerobic digestion of vinasse, several other products are released. The production of 6–8 kg granular sludge per m² of bioethanol can be sold as inoculum of UASB digesters (Upflow Anaerobic Sludge Blanket). Also, there is a release of a significant amount of solids which settle spontaneously (10 g/L of vinasse).

In Brazil, the vinasse is directly applied to the soil as a fertilizer and source of potassium. But for this practice to be efficient, a thorough soil analysis is necessary, so that the appropriate amount of vinasse can be used. Environmental agencies are limiting the quantity of vinasse per hectare (Salomon and Lora, 2009). In the case of vinasse obtained from second generation bioethanol production, it will not contain potassium and phosphorus. Thus, ultimately it will lose its advantage as a fertilizer, both in the case of direct application of the vinasse to the soil or when the solid residue after biogas production is used.

Despite the low energy output from the production of biofuels such as ethanol, methane and burning lignin when compared to the incineration of biomass, there are advantages in the conversion of biomass to biofuels, mainly related to environmental gains resulting from greenhouse gas reduction.

Brazil has a great interest in cellulosic ethanol, the aims being to making ethanol from sugarcane more competitive and expanding production without having to increase the area under sugarcane. By combining first and second generations, more ethanol is produced per planted area. Studies conducted indicate that a distillery that today produces 1 million liters of ethanol per day using sugarcane juice could, with lignocellulose biofinery technology, generate an additional 150,000 L of ethanol from bagasse. In 2025, with the technique improved, it could show an increase in production of 400,000 L recovered from bagasse (Revista Pesquisa Fapesp, 2007). Sugarcane straw is another potential source for bioethanol production and, with the prohibition of burning, it has the potential for use as a source of cellulose.

In the future, with many options for the construction of an energetic matrix, bagasse could either be used for burning to generate bioelectricity or for the production of cellulosic ethanol, and the decision will be the market, emphasizing the most profitable option.

4. Conclusions

The residues from second generation bioethanol production were used for biogas production and for heat generation using two different types of pretreatment: alkaline hydrogen peroxide and lime, and different solids concentrations.

Simulation of different scenarios has shown that the use of bagasse for energy generation by incineration was more efficient, the energy recovery being about 1.6 times higher than for the best multiple fuels production scenario. However, this greater energy potential is realised only by the production of heat. Other energy vectors, in particular liquid fuels, are of great interest and justify the development of these processes.

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References


