Low liquid-solid ratio fractionation of sugarcane bagasse by hot water autohydrolysis and organosolv delignification

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A R T I C L E   I N F O

A B S T R A C T

In this study, the fractionation of sugarcane bagasse at low liquor-solid ratio (LSR) was firstly reported. The effect of low LSR fractionation of sugarcane bagasse by hot water autohydrolysis and organosolv delignification that consume minimal amounts of water was studied to obtain a cellulosic fraction (glucans) that is suitable for conversion to ethanol. Hot water pretreated bagasse was delignified using varied process conditions: 160–190 °C, 30–150 min and LSR 3–9. The results were compared with the untreated bagasse using the same delignification conditions. The delignification of the pretreated bagasse extracted of 86.7% of lignin and produced a solid with 90.0% of glucans (190 °C for 150 min and LSR 9). A solid consisting of 82.9% of glucans with a slightly greater lignin content was obtained with a LSR 3 whilst delignification of untreated bagasse extracted 91.3 and 92.0% of lignin (87.7 and 88.4% of glucans) for LSRs 3 and 9, respectively. Low liquor–solid ratio fractionation allowed the direct separation of the hemicelluloses and lignin to produce a solid with high glucans.

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1. Introduction

Sugarcane bagasse is an important agro-industrial by-product in Brazil, India, China and Thailand. These four countries account for approximately 70% of the world's sugarcane production (FAOSTAT, 2013). Brazil, the world's largest producer of sugarcane, produced approximately 700 million tonne sugarcane during the 2010–2011 harvest (260–290 kg bagasse tonne^{-1} sugarcane at 50% moisture) (CONAB, 2003; Rocha et al., 2012). It is usually burned in sugar and ethanol mills to produce energy. In Brazil, the ethanol yield per hectare of sugarcane is actually 6000 L ha^{-1}, but it could reach 10,000 L ha^{-1} if 50% of the generated bagasse was converted to "cellulosic ethanol" (Rocha et al., 2012). Bagasse is composed of 43% cellulose, 21–23% lignin, 25–32% hemicelluloses and minor amounts of organic extractives and inorganic compounds (Area et al., 2009; Rocha et al., 2012; Vallejos et al., 2012).

Xylo-oligosaccharides from xylans rich agro-industrial waste can be used in wide range applications including their conversion to xylose, xylitol, furfural, succinic acid, additives in papermaking, ethanol, hydrogels, films and bio-based polymers (Carvalheiro et al., 2008; Sedlmeyer, 2011).

Hemicelluloses extraction performed prior to the transformation of lignocellulosic materials to biofuels, high-value bio-based chemicals or materials could improve the economic efficiency of such processes (García et al., 2011; Vila et al., 2011; Zhang and Yang, 2011). The ethanol production from lignocellulosic materials mainly includes the pretreatment of raw materials, the hydrolysis of cellulose to sugars and the conversion of sugars to ethanol. A pretreatment step is required to disrupt the carbohydrate–lignin complex and to thus allow the hydrolytic enzymes to gain access to the carbohydrates (Wyman et al., 2005; Yang and Wyman, 2008; Zhang and Shahbazi, 2011). The pretreatment process defines the cost at which the cellulose can be converted to cellulosic pulp or ethanol because it represents an important part of the total project cost (Wyman et al., 2005). Hot water pretreatment has potential

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commercial application in the biorefinery industry inasmuch as it has proved to be efficient in the extraction of hemicelluloses from various lignocellulosic materials (Carvalheiro et al., 2004, 2009; Garrote et al., 2002, 2007; Gírio et al., 2010; Romaní et al., 2010, 2011). Compared with dilute acid pretreatment, hot water pretreatment is a more environmentally friendly process that causes less corrosion of equipment and less monosaccharide degradation; hence, there are smaller amounts of inhibitors in the spent liquor resulting in a simpler and cheaper process (García et al., 2011). These processes have the potential to recover from 55 to 84% of the hemicelluloses and to produce a hydrolyzed without almost any inhibitors in the cellulose fraction used in the conversion to ethanol (Gírio et al., 2010).

In hot water pretreatment, the lignocellulosic material suffers chemical and morphological changes such as: (i) partial deacetylation of hemicelluloses and (ii) modification of the structure of lignin and its rearrangement within the lignocellulosic structure. These changes will affect the efficiency of subsequent organosolv delignification processes (McDonough, 1993).

The organosolv processes have not yet reached the commercial stage despite several trials of pilot experiments that have already been reported. These processes are based on the use of aqueous solutions of organic solvents (ethanol, acetic acid, acetone and other solvents) to remove lignin from lignocellulosic materials (Biermann, 1996; Gírio et al., 2010; Sixta, 2006). Some of their advantages are sulphur-free emissions and simple recovery process, which is suitable for relatively small mills. The organosolv delignification is controlled by pH and the ability of the solvent to participate in fragmentation reactions of the lignin (a result of the solvent's physical properties) (El Hage et al., 2010).

Currently, there is much effort in research and development to determine which pretreatment is most efficient for lignocellulosic materials (Liu et al., 2011; Rocha et al., 2012; Wyman, 2005; Yang and Wyman, 2008; Zhang, 2008; Zhang and Shahbazi, 2011). Recent articles provide an overview of several pretreatments that remove the hemicelluloses and lignin using a sequential process (Wyman, 2005; Yang and Wyman, 2008; Zhang, 2008; Zhang and Shahbazi, 2011). Details on the combination of hot water pretreatment and organosolv delignification processes of wood, grass and agro-industry waste have recently been published (Amendola et al., 2012; Garrote et al., 2003; Huijgen et al., 2012; Liu et al., 2011; Ruiz et al., 2012). These studies demonstrated the effects of the treatments on the physical and chemical properties of the paper as well as the effects of the residual solid on the saccharification process.

In the case of the use of a cellulosic fraction for ethanol production, the pretreatments are based on the extraction of the hemicelluloses and lignin to disrupt the carbohydrate-lignin complex thereby allowing the access of the hydrolytic enzymes to cellulose. Autohydrolysis pretreatment produces a partial removal of the hemicelluloses and the rearrangement of lignin on the surface of the lignocellulosic material (García et al., 2011; Kristensen et al., 2008; Yang and Wyman, 2008; Zhang and Shahbazi, 2011). The organosolv delignification of pretreated material allows the recovery of lignin as a sulphur-free, high purity and quality fraction. Gopal et al. (1992) reported that, in the autocatalysed organosolv pulping of mixed hardwoods, the residual lignin in the pulp (measured as kappa number) increased slightly when the LSR was reduced to 4.5:1. The changes in the LSR may have affected the delignification kinetics because of solubility limitations.

The reduction of water consumption mainly produces a higher concentration of dissolved components in the pretreatment's liquors (hemicelluloses and lignin), which would reduce the costs for recovery. Additionally, the reduction of water consumption in the two stage fractionation would allow a reduction in both the amount of water in the system and the operating costs. For the same amount of feedstock to be processed, this change would result in a smaller amount of solvent to remove, a lower consumption of both fresh water and steam. Therefore, the volume of both the storage tanks and the pumping systems would be reduced. The use of low values of the LSR presents economic advantages but requires modifications in the recovery of the resulting liquors because part of the treatment solution remains adsorbed in the solid fractions.

Numerous authors have reported the effect of different operating variables on organosolv pulping; however, none studied the two stage fractionation that minimizes water consumption for sequential extracting of the hemicelluloses and lignin. The aim of this work is the study of the two stage fractionation of sugarcane bagasse by hot water and organosolv treatments that minimize water consumption (i.e., have a low LSR) for the extraction of hemicelluloses and lignin to obtain a cellulosic fraction suitable for conversion to ethanol. The obtained results were compared with the organosolv delignification of the untreated sugarcane bagasse.

2. Materials and methods

2.1. Raw materials

Whole sugarcane bagasse was supplied by the Ipiranga sugarcane mill (Descalvado, State of São Paulo, Brazil). The particle size of bagasse was approximately 1–5 cm. The bagasse was characterized in a previous work (Vallejos et al., 2012).

2.2. Hot water autohydrolysis

The hot water pretreatment conditions were selected based on previous results obtained in the study of hydrothermal processes performed at mild temperatures, short times and low LSRs to assess the effect of pretreatment conditions on the concentrations of xylose and xylo-oligosaccharides in the obtained liquors (Vallejos et al., 2012). The selected experimental conditions for the present study were: 1 kg of sugarcane bagasse, 170 °C for 60 min and a LSR of 6 (g/g). The pretreatment was performed in a 23 L batch digester (Regmed HB-21, Brazil) with rotary stainless steel vessel (4 rpm).

2.3. Organosolv delignification

The organosolv delignification of pretreated and untreated bagasse was performed in a stainless steel cylindrical reactor (capacity 195 cm^3, OD 5.0 cm × ID 4.0 cm, length 15.5 cm) heated in a thermostatic glycerol bath (Marconi, São Paulo, Brazil). The water content of the bagasse was accounted for explicitly in the material balances.

Pretreated and untreated bagasse were delignified using an ethanol–water ratio of 1:1 (v/v) with varied process conditions in the ranges of 160–190 °C, 30–150 min and LSR of 3–9 (mL g^{-1}). The reactors were immediately chilled in an ice-water bath at the end of the reaction time. The residual solid and the liquid fraction were separated by filtration. The residual solid was washed with 1% NaOH and then with water until a neutral pH was reached. Finally, this material was air dried, and the yields of organosolv delignification were determined. The washing liquids were acidified with H_2SO_4 to pH 2 to precipitate the acid insoluble lignin.

2.4. Analysis of fractionated bagasse

The ash content of the pretreated bagasse was determined at 525 °C (TAPPI T211 om-02 "Ash in wood, pulp, paper and paperboard"). The pretreated bagasse was milled and sieved (<1 mm sieve) before the determination of lignin content (72 wt% H_2SO_4, at room temperature for 2 h).

Table 1
Levels of the studied parameters in a 2^3 statistical experimental design for the organosolv delignification.

Variable	Coded variable level		
	−1	0	+1
$T\,(°C)$	160	175	190
$t\,(min)$	30	90	150
LSR $(mL\,g^{-1})$	3	6	9

The acid-insoluble lignin was then filtered, dried to constant weight and weighed (TAPPI T222 om-02, "Acid-insoluble lignin in wood and pulp"). Monosaccharides (glucose, xylose, arabinose), organic acids (acetic acid, formic acid) and degradation products of monosaccharides (HMF, furfural) present in the hydrolyzed were analyzed by high performance liquid chromatography (HPLC) to determine sugars and acetyl groups (NREL – Laboratory analytical procedure: LAP-002 "Determination of Carbohydrates in Biomass by High Performance Liquid Chromatography" and LAP-004 "Determination of Acid-Soluble Lignin in Biomass").

The monosaccharides, organic acids and degradation products were determined by HPLC in a Shimadzu CR 7A chromatograph. Cellobiose, glucose, xylose, arabinose, acetic acid and formic acid were separated on an Aminex HPX 87H column (300 × 7.8 mm, BIORAD), with a Shimadzu R10-6A IR detector. The eluent was 5 mM H_2SO_4, flowing at 0.6 mL min^{-1}, at 35 °C.

The furfural and HMF were determined on a Hewlett-Packard C18 column, model RP 18, with a Shimadzu SPD-10A UV–Vis detector set to 274 nm (eluent: phase acetonitrile–water 1:8, v/v, solution and 1% acetic acid, v/v, flow: 0.8 mL min^{-1}, at 25 °C).

The weights of cellobiose and glucose were converted to glucans equivalents, the xylose to xylans, the arabinose to arabinans and the acetic acid to acetyl groups by multiplying them by the hydrolysis factors: 0.95, 0.90, 0.88 and 0.717, respectively. HMF and furfural were converted to amounts of glucans and xylans by multiplying them by 1.286 and 1.375, respectively.

The chemical composition of the residual solids obtained from the delignification reactions was determined using the same procedure.

2.5. Data analysis

A full 2^3 factorial design with two central points was carried out to assess the effect of the temperature, time at temperature and LSR on organosolv delignification of both pretreated and untreated bagasse (control) to obtain a cellulosic fraction suitable for conversion to ethanol (Table 1). The real values of the variables were transformed to coded values, so that the low, midpoint and high levels of all coded variables are −1, 0 and +1, respectively. This conversion guarantees orthogonality, so that the effect of one factor or interaction can be estimated separately from the effect of any other factor or interaction in the model, avoiding distortions in the statistical analysis.

Experiments of 10 total assays were performed (8 factorial points and 2 centre points). The coded parameters (independent variables) selected for this study are shown in Table 1.

The dependent variables studied were: yield, the chemical composition of the residual solid and the delignification percentage. The results were assessed by an analysis of variance (ANOVA) with STATISTICA 10.0 (StatSoft, Inc.) and the degree of fit was estimated from R^2, which indicates the variability of the results.

3. Results and discussion

The chemical composition of untreated sugarcane bagasse is shown in Table 2. This composition was similar to that previously

Table 2
Chemical composition of untreated and pretreated bagasse (% on dry weight basis).

Chemical composition (%)	Untreated bagasse (Vallejos et al., 2012)	Pretreated bagasse
Glucans	42.6	63.6
Xylans	24.9	10.1
Arabinans	3.43	0.79
Acetyl groups	3.63	n.d.
Lignin	21.7	26.0
Extractives	2.06	[a]
Ash	1.45	[a]

[a] Not determined.

reported by other authors (Area et al., 2009; Rocha et al., 2012; Vallejos et al., 2012).

The hot water pretreatment of bagasse was performed in agreement with the results of a previous study (Vallejos et al., 2012) that detailed the effect of low LSR hot water pretreatment of sugarcane bagasse at mild temperatures. The conditions selected for the current study were 170 °C for 60 min and a LSR of 6. Under these conditions, the spent solid yield was 74.1%, and the carbohydrate content (glucans, xylans and arabinans) in the pretreated bagasse was 74.5%.

The hot water pretreatment extracted 68.8% of xylan. The xylan removal increased the cellulose and lignin contents in pretreated sugarcane bagasse through a concentration effect (Table 2). The acetyl groups of the hemicelluloses were removed during the hot water treatment (i.e., deacetylation of hemicelluloses). The influence of the pretreatment on xylans and xylose concentrations using hot water pretreatment with low LSR on sugarcane bagasse at mild temperatures was reported in a previous work (Vallejos et al., 2012). The maximum concentrations of xylose and xylans were 13.8 and 36.2 g L^{-1}, respectively, (equivalent to 48.3 g L^{-1} of xylans) which were achieved by treating bagasse at 170 °C for 60 min, with a LSR of 3.

Tables 3 and 4 show the results obtained for pretreated and untreated bagasse, respectively. The lower overall yields were obtained at 190 °C for 150 min using a LSR of 9 (pretreated bagasse: 62.4%; untreated bagasse: 50.5%). For the same conditions, except for a LSR of 3, the yields were higher (70.0 and 51.2% for the pretreated and untreated bagasse, respectively). The reduction of LSR from 9 to 3 increased the yield as well as an increase of liquor to solid ratio improves the mass transfer and thus solubility of hemicellulose and lignin.

In mild delignification conditions (assays 1 and 2) approximately 27.0% of mass loss was achieved independent of the LSR. For the untreated bagasse, the weight loss was considerably lower depending on the LSR (11.3 and 12.9% for LSRs of 3 and 9, respectively).

Under more severe delignification conditions (assays 7 and 8), 30.0 and 37.6% of mass loss were recorded for LSRs of 3 and 9, respectively. In these conditions, 68.8 and 86.7% of the lignin content of the pretreated bagasse was extracted (LSRs of 3 and 9, respectively). The delignification of untreated bagasse led to a solubilization of 48.8 and 49.5% (relative to the original mass) for a LSR of 3 and 9, respectively; under these conditions, there was 92.0% and 91.3% of delignification, respectively. The residual lignin contents obtained from the pretreated bagasse were 11.6 and 5.6% for a LSR of 3 and 9, respectively whilst for the untreated bagasse were 3.4 and 3.7%, respectively. The decrease of the LSR at severe delignification conditions reduced the extraction of pretreated bagasse (approximately 7.6% less with respect to a LSR of 9). Under severe delignification conditions (assays 7 and 8), the residual lignin content after organosolv delignification of pretreated bagasse (Table 3) was higher than that of untreated bagasse. This showed that a lignin fraction was more resistant to extract when a LSR 3 was

Table 3
Chemical compositions of residual solids after delignification of the hot water pretreated bagasse.

Assay	T (°C)	t (min)	LSR (g/g)	Yield[a]	Glucans[b]	Xylans[b]	Arabinans[b]	Lignin[b]	D (%)
1	−1	−1	−1	73.0	77.7	8.15	0.15	13.2	63.0
2	−1	−1	1	72.7	78.6	8.16	0.18	13.2	63.1
3	−1	1	−1	71.2	80.8	8.11	0.15	11.3	69.0
4	−1	1	1	69.8	81.4	8.48	0.16	10.1	72.8
5	1	−1	−1	71.5	81.8	8.00	0.15	11.8	68.2
6	1	−1	1	69.5	82.9	8.26	0.18	9.98	73.3
7	1	1	−1	70.0	85.4	6.09	0.05	11.6	68.8
8	1	1	1	62.4	90.0	6.54	0.00	5.55	86.7
9	0	0	0	70.9	83.5	7.54	0.15	10.4	71.6
10	0	0	0	71.1	80.4	7.85	0.18	10.6	71.9

D: delignification.
[a] g of residual solids/100 g of pretreated bagasse.
[b] g of component/100 g of residual solid.

Table 4
Chemical composition of the residual solids after delignification of untreated bagasse.

Assay	T (°C)	t (min)	LSR (g/g)	Yield[a]	Glucans[b]	Xylans[b]	Arabinans[b]	Acetyl[b]	Lignin[b]	D (%)
1	−1	−1	−1	88.7	56.0	26.1	1.86	1.28	19.7	19.5
2	−1	−1	1	87.1	52.4	24.2	2.26	n.d.	18.8	24.6
3	−1	1	−1	75.8	68.1	23.7	1.44	n.d.	15.7	45.2
4	−1	1	1	72.6	57.0	23.8	1.76	n.d.	14.9	50.2
5	1	−1	−1	70.9	65.8	23.1	1.50	n.d.	14.9	51.3
6	1	−1	1	67.8	68.8	22.3	1.36	n.d.	13.6	57.5
7	1	1	−1	51.2	87.7	13.3	0.31	n.d.	3.41	92.0
8	1	1	1	50.5	88.4	12.4	0.40	n.d.	3.72	91.3
9	0	0	0	66.2	69.8	21.5	1.38	n.d.	12.1	63.1
10	0	0	0	67.9	72.0	23.0	1.36	n.d.	12.9	59.6

n.d.: no detect; D: delignification.
[a] g of residual solids/100 g of untreated bagasse.
[b] g of component/100 g of residual solid.

used. However, at LSR 9 a large part of this fraction was extracted whereby the residual lignin content was slightly higher than that of untreated bagasse. These results showed that during hot water pretreatment a xylans fraction of the bagasse is removed, which makes the resulting lignocellulose matrix more accessible for delignifying solvents at mild delignification conditions (assays 1 and 2). In case of direct one-stage organosolv, a certain pretreatment severity is needed to remove the xylans first before effective delignification can occur. The lignin deconstruction during the hot water treatment increases its extractability during the organosolv delignification. However, this lignin deconstruction is associated with condensation reactions. The extraction of the condensed lignin fraction required of severe delignification conditions (Obama et al., 2012). The two stage fractionation removes the hemicelluloses and lignin and which improves the surface area. In the case of ethanol production, the improving the surface area accessible to enzymes is a more factor important than the removal of lignin for achieving a high sugar yield (Rollin et al., 2011).

The ANOVA test for the delignification of pretreated bagasse showed that the delignification yield, lignin content and delignification per cent were significantly affected by temperature, time, the LSR and the interactions between temperature and the LSR as well as those between time and LSR ($p < 0.05$). Glucans content depended on temperature and time ($p < 0.05$). The results fail to show an adequate fit for the xylans and arabinans content (*lack of fit test* < 0.05). Further, the temperature, time and temperature/time interaction significantly affected the lignin content of the untreated bagasse ($p < 0.05$).

As previous work has shown, the organosolv processes consist of the breakdown of the lignin macromolecule before it is dissolved (Kristensen et al., 2008). Our results suggest that a significant fraction of lignin was easily removed in a way different from the conventional delignification reaction, which is dependent on temperature and time (in accordance with the Arrhenius

postulate), as it was observed in the untreated bagasse delignification. These were showed in a preliminary experiment, where sugarcane bagasse was treated by hot water pretreatment at 150, 160 and 170 °C for 60 min and a LSR of 3. The acidification of the alkaline washing liquids generated a dark precipitate of acid insoluble lignin. Therefore, the hot water pretreatment produced the lignin fragmentation so that a lignin fraction was easily dissolved in alkaline solution. These results showed that the bagasse suffered a fragmentation during the hot water pretreatment, which allowed the partial extraction of lignin with respect to the control when mild delignification conditions were used.

The acetyl groups were present only in the delignified untreated bagasse at 160 °C, 30 min and a LSR of 3, representing almost 35.0% of the initial content. The acetyl groups from untreated bagasse were completely removed under the other delignification conditions.

The standardized Pareto Chart and Main effects plot for delignification percentage of pretreated bagasse is shown in Fig. 1. The pretreated bagasse reached 86.7% delignification with high glucans
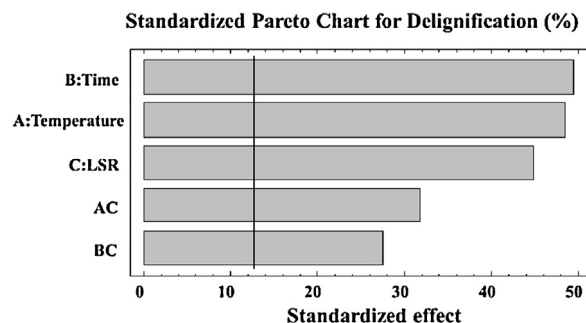

Fig. 1. Standardized Pareto Chart for delignification of pretreated bagasse.

content (90.0%) at 190 °C for 150 min and a LSR of 9. The delignification percentages for the untreated bagasse at the same conditions were 91.3 and 92.0% for LSRs of 3 and 9, respectively, with slightly lower glucans content (approximately 88%). These results showed that LSR 3 was suitable to obtain a solid fraction with high glucans content and the reduction of liquor to solid ratio or water consumption was achieved.

4. Conclusions

The combination of the hot water autohydrolysis (180 °C, 60 min and LSR 6) and organosolv delignification of sugarcane bagasse that minimize water consumption (190 °C, 150 min and LSR 3) allowed extraction of 68.8% of xylans and high lignin fraction (68.8%) and produced a solid with a high content of glucans (85.4%). Under the same conditions, the delignification of untreated bagasse extracted 92.0% of lignin and achieved 87.7% of glucans. The direct separation of the hemicelluloses, lignin and cellulose was obtained at low LSR fractionation. An effective separation of the three components is achieved, although delignification obtained is lower than that achieved at higher liquid to solid ratios.

Acknowledgements

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