Optimization of the acetosolv extraction of lignin from sugarcane bagasse for phenolic resin production

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ABSTRACT

The experimental central composite design 2^2 was applied to optimize the acetosolv process for lignin extraction from sugarcane bagasse, with an aim to replace the petroleum-derived phenols conventionally used for resin production. The highest acetosolv extraction yield ($55\% \pm 4.5\%$) was achieved with an acetic acid concentration of 95% (w/w), containing 0.1% (v/v) HCl, at 187 °C for 40 min. Other optimal conditions for extraction, such as 187 °C, 15 min ($OC_{187;15}$) and 205 °C, 15 min ($OC_{205;15}$), were calculated from statistical models. The optimized acetosolv lignins were characterized by thermal analysis (TGA and DSC), size exclusion chromatography, and spectroscopic methods (FT-IR and HSQC-NMR). Compared to Kraft lignin, they exhibited higher thermal stability, low molar mass, *p*-hydroxyphenyl units as their major constituent, higher relative phenolic and total hydroxyl contents, and lower relative methoxyl group content. Accordingly, optimized acetosolv lignins seem to have structural features suitable for phenol-formaldehyde resin synthesis.

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1. Introduction

The use of renewable resources by industries has been growing in recent years with an aim to increase economic and environmental efficiency. However, development of new technologies is required to expand the use of lignocellulosic biomass for the production of high value-added products within the biorefinery concept (Ragauskas et al., 2014). Among the various lignocellulosic biomass materials available, sugarcane bagasse is one of the most abundant. The most recent data released by the Food and Agriculture Organization of the United Nations (FAO, 2015) show that in 2013, the global production of sugarcane was 1.9×10^9 t, resulting in the production of approximately 0.28×10^9 t of bagasse as a by-product of the cane-sugar industry (Chandel et al., 2012).

This lignocellulosic material is partially used in sugar and ethanol production plants to generate thermal energy. However, bagasse contains between 18% and 27% of lignin (Sun et al., 2004; Costa et al., 2014). Energy can still be generated via second-generation ethanol production from the remaining holocellulose, after lignin extraction. The remaining fiber will be more accessible to the enzymes because the physical barrier that hinders hydrolysis is removed.

Lignin is a macromolecule, mainly composed of guaiacyl, syringyl and *p*-hydroxyphenyl units, which differ by the presence or absence of *ortho*-methoxyl groups in the aromatic rings. Owing to the presence of these phenolic groups in its molecule, lignin has a wide range of applications in the chemical industry and can be used for the production of carbon-fiber, polyurethane, rubber, polypropylene, and phenol-based chemicals (Lora and Glasser, 2002). Lignin can also be used as a partial substituent of phenolic resins, which helps to reduce the presence of toxic substances in the final product obtained from petroleum-based resins (Ghaffar and Fan, 2014; Ragauskas et al., 2014).

Table 1

Relative absorbance values of functional groups (RA_{TOH}, RA_{FOH}, and RA_{OCH3}), extraction yield (Y_{AE}), production of lignin (P_{Lig}), weighted-average molar mass ($\bar{M}w$), number-average molar mass ($\bar{M}n$), and polydispersity ($\bar{M}w/\bar{M}n$)of the acetosolv lignins (L1–L11), Kraft lignin (KL) and the lignins extracted at optimum conditions ($OC_{T,t}$).

Experiment	T (°C)	t (min)	P_{Lig} (g_{Lig}/g_{Fibre})	Y_{AE} (%)	RA_{TOH}	RA_{FOH}	RA_{OCH3}	$\bar{M}w$ (g/mol)	M̄n (g/mol)	$\bar{M}w/\bar{M}n$
L1	103	28	0.066	22.2	12	0.6	0.24	6013	747	6.4
L2	187	28	0.152	50.8	13	0.78	0.15	3438	523	7.4
L3	103	92	0.116	38	12	0.56	0.23	6669	724	7.7
L4	187	92	0.158	52.8	20	0.75	0.15	4319	513	8.6
L5	145	60	0.168	56	11.5	0.6	0.2	3461	428	9.3
L6	145	60	0.153	51	11	0.6	0.17	5276	523	9
L7	145	60	0.160	53.6	13	0.77	0.18	4395	511	8
L8	85	60	0.076	25.4	11	0.58	0.26	7775	967	4.5
L9	205	60	0.184	61.6	19	0.78	0.13	7556	369	13.7
L10	145	15	0.167	55.7	13	0.6	0.17	5199	579	8.7
L11	145	105	0.157	52.5	12	0.6	0.18	4746	532	11.2
$OC_{187;40}$	187	40	0.166	64.3	11.6 ± 1.1[a]	0.57 ± 0.03[a]	0.12 ± 0.01[a]	2438	312	7.8
$OC_{187;15}$	187	15	0.192	55.6	12.6 ± 0.94[a]	0.61 ± 0.06[a]	0.14 ± 0.001[a]	2480	248	10
$OC_{205;15}$	205	15	0.164	55	12.4 ± 1.2[a]	0.56 ± 0.004[a]	0.12 ± 0.01[a]	1494	339	4.4
KL	–	–	–	–	46	1.14	0.44	–	–	–

[a] Values after "±" refers to Confidence Interval (CI) of 95%. $OC_{T;t}$ refers to the optimal condition at temperature T and reaction time t. KL refers to Kraft lignin.

The structure of lignin differs depending on the isolation process (Kraft, sulfite, or organosolv). The functional groups and molecular weight also vary among the different types of lignin. Despite Kraft and sulfite processes being the most used in the pulp and paper industries, these types of lignin have low reactivity owing to the presence of impurities in high quantities (Wild et al., 2014), which, in turn, decreases its industrial applications. Alternatively, the organosolv process uses organic acids and/or alcohols as delignification agents. With this process, it is possible to extract lignin with high purity and reactivity, while ensuring efficient solvent recovery (Zhao et al., 2009).

The organosolv process has been widely used for lignin extraction from several lignocellulosic biomasses, including sugarcane bagasse (Ramires et al., 2010; Mesa et al., 2011). Nevertheless, to our knowledge, no reports have been published on the use of an experimental design for optimization of the acetosolv process, with an aim to extract lignin from sugarcane bagasse for phenolic resin production. In the organosolv process, protolignin, which is the complex structure present in the vegetal, is attacked by species in the reaction medium, following which the ether bonds are broken and less complex and more soluble structures are obtained (Sridach, 2010). In this work, the evaluation of the acetosolv parameters was based on the extraction yield and on the quantification of functional groups that are relevant for phenol-formaldehyde resin production. Furthermore, we determined the structural and thermal characteristics of the lignins extracted by the experimental organosolv process.

2. Material and methods

2.1. Biomass: sugarcane bagasse

Sugarcane bagasse was donated by an alcohol and spirits industry located in Ceará State, Brazil. Owing to the high moisture content of the bagasse, it was stored in a freezer at −18 °C. Prior to the experiments, the bagasse was freeze-dried, ground, and sieved (18 mesh or 1 mm). The sugarcane bagasse used in this study contained cellulose (36.4%), hemicellulose (20.1%), lignin (29.9%), extractives (6%), and ash (5.4%).

The characterization of the milled sugarcane bagasse was based on TAPPI T203 cm-99 (TAPPI, 2009), TAPPI T204 cm-97 (TAPPI, 1997), TAPPI T222 om-02 (TAPPI, 2002a), TAPPI T413 om-93 (TAPPI, 1993a), TAPPI T412 om-93 (TAPPI, 1993b) and TAPPI T421 om-02 (TAPPI, 2002b) for determination of moisture, ash, extractives, lignin, and alpha-cellulose, respectively. The contents of holo-

cellulose and hemicellulose were determined by the procedure described by Yokoyama et al. (2002).

The alkaline lignin used for comparison in this study was purchased from Sigma Aldrich.

2.2. Acetosolv process

Extraction of lignin by the acetosolv process was performed with various concentrations of acetic acid and with HCl 0.1% (w/w) as the catalyst (Xu et al., 2006). The extractions were performed in mini high-pressure reactors (Berghof high preactor BR-300), with a total volume of 500 mL. Preliminary results of lignin extraction (not shown) indicated that the best acetic acid concentration was 95% (w/w) and the best fiber mass per volume of reagent ratio was 1:20. The total volume of the solution in the reactor was 200 mL.

2.3. Experimental design and statistical analysis

Determination of the temperature and reaction time at which lignin extraction yield from sugarcane bagasse was the maximum was performed with the aid of a central composite design 2^2 (two levels and two independent variables), with the central point (level 0) in triplicate and four star points. It was applied to the surface response method for analysis of the effects of reaction time (t) from 15 to 105 min and temperature (T) from 85 to 205 °C on extraction yield (Y_{AE}), specific lignin production (P_{Lig}), relative absorbance of total hydroxyl groups (RA_{TOH}), relative absorbance of phenolic hydroxyl groups (RA_{POH}), relative absorbance of methoxyl groups (RA_{OCH3}), weight-average molar mass ($\bar{M}w$), and number-average molar mass ($\bar{M}n$). Using this model, it was possible to evaluate the linear and quadratic effects of the variables on the lignin extraction process. All dependent and independent variables are shown in Table 1.

2.4. Lignin isolation

Lignin contained in black liquors derived from the acetosolv processes was pre-concentrated on a rotary-evaporator and precipitated in water at 60 °C, at a black liquor to water ratio of 1:10 (Bennar et al., 1999). After leaving the solution at rest for 24 h, filtration was performed to separate the lignin fraction from the sugar liquor by using a paper filter, with a porosity of 8 μm. After filtration, the paper filter containing lignin was dried at 60 °C for 24 h.