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Optimum operating conditions for brewer's spent grain soda pulping

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Abstract

The soda pulping of brewer's spent grain (BSG) pretreated with dilute-acid was studied. A first-order full-factorial design was used to evaluate the effect of the operational variables: soda concentration (1–2%), temperature (80–120 °C) and pulping time (30–90 min), on the properties of the pulp (cellulose and lignin contents) obtained from BSG. The factorial design permitted to identify the optimum operating conditions for BSG soda pulping. Equations relating the responses (properties of the pulp) to the operational variables were thus proposed, and fitted the experimental results at 99 and 90% confidence levels, for the cellulose and lignin contents, respectively. The best pulping conditions (2% soda concentration, 120 °C, 90 min) led to a pulp containing 72.1% w/w cellulose and low residual lignin content (10.4% w/w).

Keywords: Brewer's spent grain; Soda; Pulp; Lignin; Cellulose; Statistical methodology

1. Introduction

In the worldwide, around 95% of all raw materials used by the paper industry to obtain cellulose pulp consists of hardwood or softwood. The other raw materials used for this purpose are known as 'non-wood' materials (Jiménez, Ramos, Rodríguez, de la Torre, & Ferrer, 2005). Although cellulose pulps are mainly obtained from woods, several authors report that the production of pulp from non-wood resources has several advantages such as easy pulping capability, excellent fibers for the special types of paper and high-quality bleached pulp (López, Ariza, Pérez, & Jiménez, 2000; Navaee-Ardeh, Mohammadi-Rovshandeh, & Pourjoozi, 2004). In addition, considering the current increase of the concern about forests preservation and rational use of their residues, the use of non-wood plants for obtainment of cellulose pulps contributes to decrease the use of forest wood resources. Non-wood pulps can be used as such, or mixed with pulp from wood or recycled paper to obtain various products such as paper, cardboard and other lignocellulosic derivatives (Jiménez, Pérez, de la Torre, & Garcia, 1999; López et al., 2000).

Among the treatment processes for obtainment of cellulose pulps, there is a predominance of sulfate (Kraft) and sulfite methods, which makes up two-thirds of the world production of paper pulps (Fengel & Wegener, 1989). However, the use of sulfurated chemical agents in these methods brings with a serious environmental impact due to the released sulfur compounds, and the bleaching with chloride derivatives that produce highly toxic organochloride compounds (Iglesias, Bao, Lamas, & Vega, 1996). Nowadays, there is a great interest for new pulping systems that avoid or reduce the use of chemical agents, which alone or interacting with the lignocellulosic material could produce a serious environmental impact. The use of soda solutions constitutes an alternative method for producing chemical or semi chemical pulps from non-wood lignocellulosic materials, without this problem (Iglesias et al., 1996; Xiao, Sun, & Sun, 2001). Besides, a pulping process performed with high efficiency led to a reduction in the amount of chemical reagents necessary for pulp bleaching and a concomitant reduction in the pollutants discharged from bleach plant (Zhao, Li, Qu, & Gao, 2002). However, delignification processes and the resulting pulps are influenced by several parameters such as the raw material, solid:liquid ratio, cooking time, temperature and concentration of the cooking chemicals, the last one being considered the most important for lignin and polysaccharide dissolution (Fengel & Wegener, 1989). For this reason, the optimum soda pulping operational conditions must be established to each raw material used.

In recent years, the pulping potential of various non-wood materials has been examined (Iglesias et al., 1996; Jiménez

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et al., 2005; Navaee-Ardeh et al., 2004; Xiao et al., 2001). Brewer's spent grain (BSG), the main brewery by-product, is a lignocellulosic material that could be used for several applications, but it is basically used as animal feed (Mussatto, Dragone, & Roberto, in press). The cellulose pulp production could be an interesting alternative for BSG use. In the present work, BSG was initially submitted to a dilute-acid hydrolysis process aiming to solubilize the hemicellulosic fraction. Subsequently, the obtained solid residue (basically cellulignin) was subjected to a soda pulping to solubilize the lignin, producing a cellulose-rich residue. An experimental design was used to evaluate the effect of the operational variables (soda concentration, temperature and pulping time) used for BSG soda pulping, on the properties (cellulose and lignin contents) of the prepared pulp.

2. Material and methods

2.1. Raw material obtainment and pretreatment

BSG was supplied by the microbrewery of the Faculty of Chemical Engineering of Lorena. Prior to be used in the pulping process, the BSG was submitted to a pretreatment with dilute sulfuric acid under the conditions optimized by Mussatto and Roberto (2005), which were based on the use of 100 mg acid per gram of dry matter, a solid:liquid ratio of 1:8 g:g, at 120 °C for 17 min. After the reaction, the obtained solid residue was separated by centrifugation, washed with water until neutral pH and dried at 50 ± 5 °C to attain around 50% moisture content. The original material and the acid pretreated BSG were chemically characterized to determine the cellulose, hemicellulose and lignin contents.

2.2. Soda pulping process

The acid pretreated BSG solid residue was submitted to pulping reactions, which were carried out in 200-ml stainless steel batch cylindrical reactors. Reactions were performed using the BSG and the soda solution in a solid:liquid ratio of 1:20 g:g, at different soda concentrations, temperatures and pulping times, according to a 2^3 full factorial design (Table 1). Under the required temperature, the dully-covered reactors (filled with the BSG and the soda solution) were introduced into a silicone oil bath (with recirculation and temperature controller) where they were maintained during the desired time. At the end of each reaction, the reactors were immediately cooled in ice bath. The black liquor was thus separated from the pulp by filtration in a 100% polyester cloth. The pulps were exhaustively washed with water to remove residual alkali, and after drying at 50 ± 5 °C, a sample of each obtained pulp was analyzed to determine the remaining cellulose, hemicellulose and lignin contents. All the reactions were carried out in duplicate.

Table 1
Experimental ranges and levels of the process independent variables according to a 2^3 full factorial design

Independent variable	Symbol	Range and levels		
		−1	0	+1
Soda concentration (% w/v)	X_1	1.0	1.5	2.0
Temperature (°C)	X_2	80	100	120
Pulping time (min)	X_3	30	60	90

2.3. Experimental design

A 2^3 full-factorial design with three coded levels leading to 11 sets of experiments was made to evaluate the effect of three different variables: soda concentration (X_1), temperature (X_2) and pulping time (X_3) during the BSG pulping. For statistical analysis, the variables were coded according to the Eq. (1), where each independent variable is represented by x_i (coded value), X_i (real value), X_0 (real value at the center point), and ΔX_i (step change value). The range and the levels of the variables investigated in this study are given in Table 1. Three assays in the center point were carried out to estimate the random error needed for the analysis of variance, as well as to examine the presence of curvature in the response surface. The residual lignin and the cellulose content in the obtained pulps were taken as the dependent variables or responses of the design experiments.

$$x_i = \frac{(X_i - X_0)}{\Delta X_i} \quad (1)$$

Experimental data were fitted to the first-order polynomial Eq. (2), where $\hat{y}_i$ represents the response or dependent variable; b_0 is the interception coefficient; b_i, b_{ii}, and b_{ij} are the regression coefficients; n is the number of variables studied; and X_i and X_j represent the variables.

$$\hat{y}_i = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j \quad (2)$$

Statistica 5.0 (Statsoft, USA) software was used for regression and graphical analyses of the obtained data. The statistical significance of the regression coefficients was determined by Student's t-test, and the proportion of variance explained by the model was given by the multiple coefficient of determination, R^2.

2.4. Analytical procedures

The cellulose, hemicellulose and lignin contents in the BSG samples were determined according to standard methods (Browning, 1967). Micrographs of BSG particles were obtained by scanning electron microscopy (SEM) using a LEO1450VP microscope (Schott Zeiss do Brasil Ltda, São Paulo, Brazil).

3. Results and discussion

3.1. BSG acid pretreatment

To be used in the pulping process, BSG was initially pretreated with dilute sulfuric acid to solubilize the hemicellulosic fraction. The previous removal of the