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Influence of temperature, time, liquid/solid ratio and sulfuric acid concentration on the hydrolysis of palm empty fruit bunches

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HIGHLIGHTS

- Hydrolysis process of empty fruit bunches.
- Use of polynomial models to reproduce the experimental results.
- Optimization of hydrolysis operating conditions for EFB using polynomial models.
- Comparison of pulp properties of EFB and hydrolyzed EFB solid fraction.

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ABSTRACT

The influence of temperature (150–190 °C), time (0–20 min), liquid/solid ratio (6–8) and sulfuric acid concentration (0.1–0.5%), on the hydrolysis of palm empty fruit bunches (EFBs) was studied and the liquid and solid fractions were analyzed. Polynomial models were found to reproduce the experimental results with errors less than 15% in most of the cases (except for xylose concentration).

Operating conditions of 190 °C for 15 min at a liquid/solid ratio of 6 and a sulfuric acid concentration of 0.1% resulted in the production of 3.12, 4.0, 2.35 and 2.28 g/L of glucose, xylose, arabinose and acetic acid, respectively, starting with 1000 g of EFBs. The yield was 67.96%.

Soda-anthraquinone, ethanol and ethanolamine pulping of the solid fraction provided pulps with brightness values (63.24%, 28.78%, 48.76%), but with poor resistance properties (6.57–8.54 Nm/g for tensile index, 0.38–0.44 k N/g for burst index and 0.96–1.02 mN m^2/g for tear index). Therefore it is advisable to use the pulps for speciality papers or for bioethanol-production.

1. Introduction

Non-wood plants constitute an effective alternative to wood for production of cellulose derivatives (pulp for paper, dissolving pulp, sugars by hydrolysis, bioethanol by hydrolysis of cellulose and later fermentation) in countries with limited forest resources.

A promising non-wood raw material are empty fruit bunches (EFBs), a residue of the palm oil industry (Jiménez et al., 2009a,b; Rodríguez et al., 2008; Ferrer et al., 2011).

Conventional methods for producing cellulose also remove hemicelluloses and lignin. Such components can be recovered by using various procedures commonly associated with the concept of "bio-refinery" (Pan et al., 2005; Garrote et al., 2007a; Kadam et al., 2008; Requejo et al., 2012). The bio-refinery or fractionation of lignocellulosic materials as agri-food residues is especially interesting since it endows an added value and provides an environmental benefit (Sasaki et al., 2003; Sakaki et al., 2006; Garrote et al., 2007a; Kadam et al., 2008; Sánchez et al., 2011; Requejo et al., 2012).

One fractionation procedure involves the hydrolysis of lignocellulosic material and pulping of the resulting solid fraction. Hydrolysis with water at a high temperature produces an aqueous fraction essentially containing hemicellulosic sugars consisting of monosaccharides (xylose, glucose, arabinose) and xylo-oligosaccharides (Caparrós et al., 2007, 2008a,b; Alfaro et al., 2009; Yáñez et al., 2009), which can be further hydrolyzed and fermented to obtain various products (Boussarsar et al., 2009; Dogaris et al., 2009; Sakaki et al., 2006; Vázquez et al., 2007). The solid fraction composed largely of lignin and cellulose is potentially amenable to pulping for paper production (Caparrós et al., 2007, 2008a,b; Sánchez et al., 2011; Requejo et al., 2012), or for other uses such as the production of bioethanol by hydrolysis of the pulp and subsequent fermentation of glucose (Zhang and Lynd, 2010; Qing and Wyman, 2011; Requejo et al., 2011, 2012).

Hydrolysis can be conducted over wide ranges of operating conditions (Garrote et al., 2007b; Vegas et al., 2008; Sundqvist et al.,

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2006). In a weakly acidic medium, ether bonds in lignin are broken above 160–180 °C and cellulose starts to depolymerise above 210 °C. Process time can also vary from a few seconds to several hours. The liquid/solid ratio can be set at values from 2 to 40 g water/g material, but usually falls within the range 8–10 g/g. The pH has a strong influence on cellulose degradation. Particle size is also influential and usually ranges from 0.5 to 10 mm in laboratory tests.

Pulping processes applied to non-wood, mainly used soda, soda-anthraquinone and various organic solvents (López et al., 2006; Rodríguez and Jiménez, 2008; Jiménez et al., 2009a; Ligero et al., 2008; Ziaie-Shirkolaee et al., 2008; Caparrós et al., 2008b; Jiménez et al., 2007).

In the present study, the influence of operating variables on the composition of the liquid and solid fractions were studied. The solid fraction were obtained soda, ethanol and ethanolamine pulping and the properties of the pulp and paper obtained were compared with those pulp and paper obtained from raw material without prior hydrothermal treatment.

2. Methods

2.1. Raw material

EFB from *Elaeis guineensis* were supplied by Straw Pulping Engineering S.L. (Zaragoza, Spain) and their holocellulose, α-cellulose, lignin, ethanol–benzene extractives and ash contents were determined according to Tappi standards T-9 m-54, T-203 OS-61, T-222, T-204 and T-211, respectively.

Fiber length was determined biometrically, under a Visopan projection microscope, after microcooking the raw material with 10% soda at 80 °C for 1 h and subsequent staining with 1% safranin.

2.2. Hydrolysis

EFB and water required to obtain an appropriate liquid/solid ratio were placed in a 15-L batch reactor that was heated by an outer jacket containing electrical wires. The reactor contents were stirred by rotating the reaction vessel via a motor connected through a rotary axle to a control unit that also measured and controlled pressure and temperature. Once the mixture was heated to the selected temperature for the pre-set time, the reactor was depressurized, and the liquid and solid fractions were separated. The temperature profiles for the heating and cooling stages corresponded to standard operational conditions (Requejo et al., 2012).

2.3. Characterization of the fractions of the hydrolysis process

Glucose, xylose, arabinose and acetic acid contents of the liquid were determined as follow. An amount of 10–20 g of liquid fraction was placed in a 100-mL ISO bottle and supplied with sulfuric acid to a 4%. Then, the bottle was autoclaved at 121 °C at 2 atm for 20 min, cooled to room temperature with water, and its contents were analyzed by HPLC (Refractive Index Detector, Aminex HPX-87H column eluted with 0.01 M H_2SO_4, 0.6 mL/min flow rate).

The solid yield from the solid fraction was determined gravimetrically.

2.4. Pulping process

The raw material or raw material hydrolyzed was cooked with soda-anthraquinone, ethanol or ethanolamine in a 15-L batch reactor (Table 1). The cooked material was unloaded into a washer to remove residual cooking liquor and fiberised in a disintegrator at 1200 rpm for 30 min, after which the pulp was beaten in a Sprout-Bauer refiner and passed through a screen of 0.16 mm mesh size to remove uncooked particles.

2.5. Characterization of pulp and paper sheets

Pulping yield was determined gravimetrically and viscosity and Kappa number were measured in accordance with UNE 57-039 and UNE 57-034, respectively.

Paper sheets were obtained by using an Enjo-F39.71 sheet former and characterized in terms of tensile index, burst index, tear index and brightness in accordance with UNE standards (57-054, 57-058, 57-033 and 57-062, respectively).

2.6. Experimental design

The experimental design consisted of a series of points (tests) around a central composition point (central test) that were used to estimate the quadratic terms of a polynomial model (Montgomery, 1991).

The total number of tests required for the three independent variables studied in hydrolysis process (*viz.* temperature (T), time (t) and liquid/solid ratio (R) or sulfuric acid concentration (S)) was 15.

The values of the independent variables were normalized by using the following equation to facilitate direct comparison of coefficients and expose the individual effects of the independent variables on each dependent variable:

$$X_n = 2\frac{X - \overline{X}}{X_{\max} - X_{\min}}$$

where X_n is the normalized value of T, t, R or S; X is the absolute experimental value of the variable concerned; $\overline{X}$ is the mean of the extreme values of X; and $X_{\max}$ and $X_{\min}$ are its maximum and minimum value, respectively.

Experimental data were fitted to a second-order polynomial, which relates each dependent variable (solid yield, glucose, xylose, arabinose and acetic acid) with the operational variables (temperature, time and liquid/solid ratio or sulfuric acid concentration).

Table 1
Pulping conditions of EFB and of solid fraction from EFB hydrolyzed.

Raw material and pulping	Denomination	Temperature (°C)	Time (min)	Reactive (%)	Liquid/solid ratio (w/w)
EFB and soda-AQ	EFB-SA	170	30	15% Soda, 1% AQ	10
EFB-H hydrolyzed and soda-AQ	EFB-H-SA	170	30	15% Soda, 1% AQ	10
EFB and ethanol	EFB-E	170	30	60% Ethanol	10
EFB hydrolyzed and ethanol	EFB-H-E	170	30	60% Ethanol	10
EFB and ethanolamine	EFB-EA	170	30	60% Ethanolamine	10
EFB hydrolyzed and ethanolamine	EFB-H-EA	170	30	60% Ethanolamine	10