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HYDROLYSIS AND SEPARATION OF LIGNOCELLULOSIC BIOMASS IN A SULPHITE PROCESS TO VALORISE THE MAIN FRACTIONS WITHIN THE BIOREFINERY CONCEPT

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ABSTRACT: Physico-chemical and biological processes can be used to transform different pulp and paper industries through integrated forest biorefineries in order to valorise all of the main fractions of the lignocellulosic biomass (cellulose, hemicellulose and lignin). In this work, hydrolysis and fractionation processes have been studied in a sulphite pulp mill to obtain not only dissolving pulp from the cellulose but also lignosulphonates from the lignin and fermentation products from the hemicellulose. Delignification and hydrolysis experiments have been carried out at laboratory scale in order to increase the valorisation opportunities and trying to decrease the inhibitors in the final by-product. In addition, detoxification or separation treatments have been developed in order to separate the lignosulphonates and other inhibitors from the sugar substrate.
Keywords: biorefinery, sulphite pulping, hydrolysis, lignosulphonates, sugars, detoxification

1. INTRODUCTION

Biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, and chemicals) and energy (fuels, power, heat) via biochemical, thermo-chemical, chemical or mechanical processes [14]. In this sense, lignocellulosic biomass, consisting of three major fractions: cellulose (35-50% dry weight), hemicelluloses (20-35%) and lignin (10-25%) [4], shows a high interest in biorefinery and several related industries as pulp and paper mills can be transformed into forest biorefineries [11].

Among the pulping processes, the acid sulphite process is based on the extraction of cellulose by the attack under acidic conditions (pH of 1.35 ± 0.15) in the presence of excess free SO_2 [14]. The main advantages of this process are (i) the production of a high-purity cellulose (dissolving pulp) for not only textile fibre production but also for high value-added films, plastics and coatings among others [14], and (ii) the possibility to obtain a high separation of all of the main components, cellulose, hemicellulose and lignin [7]. In addition, lignosulphonates are formed during the process, showing several applications as plasticizers and additives in construction.

During the first step of the process, due to the heterogeneous nature of the lignocellulosic biomass, in addition to sugars, other decomposition products can be obtained and they can act as inhibitors in the fermentation process. Therefore, detoxification processes should be added to the process to valorize all of the fractions and to decrease the quantity of inhibitors [4].

In this work, a sulphite pulp mill is studied in order to be transformed into a forest biorefinery. Delignification, hydrolysis and detoxification processes have been developed in order to separate the three main fractions: lignosulphonates from the lignin, dissolving pulp from the cellulose and sugars from the hemicellulose.

2. MATERIALS AND METHODS

Industrial samples from a sulphite pulp mill in the north of Spain (Torrelavega) have been used. Free, total and combined SO_2 were determined according to the titration method Tappi T604 with iodine and sodium hydroxide. Sugar content (glucose, xylose, arabinose, rhamnose and galactose), acids (acetic, levulinic and formic) and other decomposition products (furfural and hydroxymethyl furfural) were measured by a Shimadzu Prominence HPLC with SHODEX SH1011 and CHO-782 columns and Refraction Index detector according to Llano et al. [7] method using 0.5mL/min of 0.005M H_2SO_4 as a mobile phase, 60°C in the oven and 198 psi of column pressure. Metals Mg^{+2} and Ca^{+2} were analyzed by flame atomic absorption spectrometer; and UV-Vis spectrophotometer was used for low molecular phenolics and lignosulphonates. All samples were analyzed in triplicate.

Hydrolysis and delignification experiments were carried out in 1-liter digesters. Overliming experiments with $Ca(OH)_2$ or NH_4OH were conducted in 250 mL erlenmeyer flasks at different pHs, times and temperatures. Granular activated carbon and powdered black carbon were used in the adsorption treatments. On the other hand, Dowex 50WX2 cation exchange resin in H^+ form and Amberlite IRA-96 anion exchange resin in OH^- form were used according to Fernandes et al. [11]. Experiments were carried out at batch mode in a rotary shaker at 60 rpm, room temperature at different settling times.

3. RESULTS AND DISCUSSION

Figure 1 shows the chemical characterization of the spent liquor obtained in the factory as a first step to study the possibilities to be transformed in a forest biorefinery [13]. The liquor is composed mainly of lignosulphonates (~60%) and sugars (~35%). Based on the obtained chemical composition of the spent liquor, a literature search was carried out to establish the possible valorization options. According to the studied references, the detoxification methods and the current processes, the main valorization options for the spent liquor are the production of lignosulphonates, xylitol, ethanol, polyhydroxybutyrate, polybutylene-succinate, furfural and/or hydrogen. In addition, other minority alternatives can be acetic acid, methanol and vanillin [13].

In order to optimize the valorization options of the factory, the second step was the study of the delignification process, maximising the quantity of sugars and lignosulphonates and minimising the inhibitors in the spent liquor. A set of digestion experiments were carried out at laboratory scale in 1-liter digesters. Different process variables were modified with this purpose: total SO_2 content of fresh liquor, fresh liquor-to-wood ratio, heating rate and maximum temperature. Heating rate affects the depolymerisation grade and the sugars content in spent sulphite liquors, whereas total SO_2 and maximum temperature affect the delignification grade and consequently the lignosulphonates of the liquor.
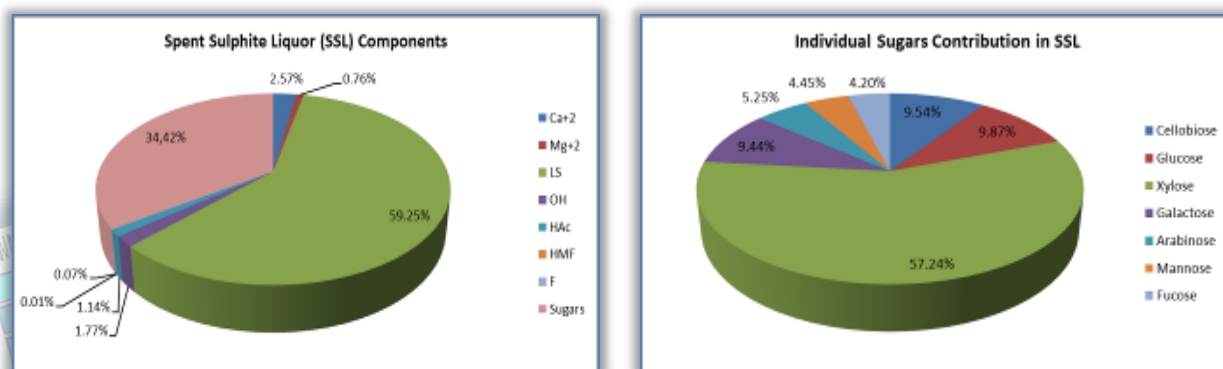

Figure 1. Characterization of the spent sulphite liquor (% w/w). LS (lignosulphonates), OH (phenolics), HAc (acetic acid), HMF (Hydroxymethilfurfural), F(furfural).

The best results were obtained at 150°C and 20-1 liquor-to-wood ratio, low heating rates and using a total SO_2 content of 6.20% [7, 10]. Once the main variables were optimized, a model of the digestion process was carried out. Maximum release of sugar and the time necessary to obtain it are shown in table 1 with and without pulp with desired quality results. If the digestion process is carried out without obtaining pulp, the maximum release are 49.41% at 130°C, 37.11% at 140°C and 32.62% at 150°C; however, the necessary time for each temperature decrease a lot among them, from 2920 minutes to 770 minutes. On the other hand, to optimize the industrial process it is necessary to use conditions, which do not degrade the pulp and obtain the maximum sugar

content in the spent liquor. Therefore, if 150°C is used as temperature of work, the maximum conversion in total sugar found in the spent liquor would be 19.22%. If the temperature of work is 140°C the release would be 17.30% and finally for 130°C would be 21.08% [13].

Table 1. Results of sugar release according to the simulation process

T (°C)	SUGAR RELEASE (%)	
	With pulp	Without pulp
150	19.22 (200min)	32.62 (770min)
140	17.30 (300min)	37.11 (1410min)
130	21.08 (600min)	49.41 (2920min)

Once the digestion process was optimize, the third step was the study of a possible external hydrolysis of the liquor in order to increase the quantity of monomers from the hemicellulose content. In this case, a factorial design of a total of 24 experiments and 3 central points was carried out. Total sugar was calculated as the sum of glucose, xylose, arabinose, mannose and galactose. Inhibitors were weak acids and furfurals [7]. A multiple regression analysis was carried out to obtain the relation among all the variables. The obtained equations were the following:

(i) Sugars (g/L)=26.5+0.017·A-13.5·B-0.0053·C-0.0029·D;

(ii) Inhibitors (g/L)=8.4+0.036·A-4.41·B+0.0057·C-0.0006·D;

(iii) LS (g/L)=96.8-0.0292·A-74.2·B+0.327·C-0.024·D,

where A is temperature, B is liquid-to-wood ratio, C is the concentration of SO2 and D time. The regression coefficients were R^2= 92.50%, 90.79% and 84.04%, respectively [7].

Finally, the last step of this work was to study different detoxification options in order to separate both lignosulphonates and sugars and to give a lower concentration of inhibitors in the sugar substrate. Overliming, Ionic exchange resins and adsorption methods were used. Figure 2 shows a comparison among all of the processes. Regarding the total inhibitor removal, most promising techniques are anionic resins at 1.5 mL/g whereas the best selectivity and therefore sugars-to-inhibitors ratio were found using overliming or anionic resin at 6 mL/g. Separation by ionic resins was proposed as the best solution, using a maximum of 6 cycles of regeneration. However, depending on the fermentation process, overliming and/or adsorption techniques can be used [8]. In this sense, an economic evaluation of the processes was performed following standard methods described by Peters et al. [9] and Turton et al. [15]. Table 2 shows the obtained results. The overliming does not appear in the table because its capital investment is low compared to the rest of techniques. It requires a tank which promotes the homogenisation of the $Ca(OH)_2$ and the liquor. According to the Fixed Capital Invested (FCI) results, resins are the best alternative; however, the Manufacturing Costs (COM) are higher when resins are used than adsorption.

Table 2. Economical results of the detoxification/separation processes

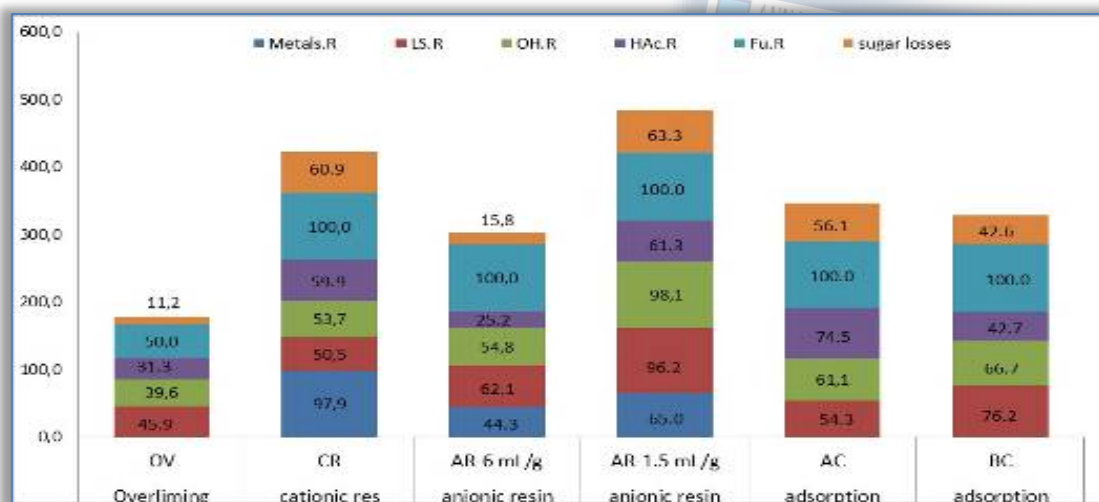| Detoxification/Separation process	FCI (M€)	COM (M€/year)
Anionic Resins	1.08	5.48
Black Carbon	2.06	2.35
Activated Charcoal	1.55	2.24
Overliming	~~	0.11

Figure 4.Results of detoxification/separation processes
OV (overliming), CR (cationic resin), AR (anionic resin), AC (activated carbon), BC (black carbon)

4. CONCLUSIONS

In this work, an acid sulphite pulping process has been studied in order to be integrated in a forest biorefinery, obtaining dissolving pulp from the cellulose, lignosulphonates from the lignin and sugars from the hemicellulose. Delignification and hydrolysis experiments have been optimized increasing the valorization options and decreasing the inhibitors in the liquor. On the other hand, ionic exchange resins are proposed as the best solution to detoxify the sugar substrate and to separate the lignosulphonates; however, an optimisation of the manufacturing costs is recommended in this case.

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