

Research Article

Evolution of Lignocellulosic Macrocomponents in the Wastewater Streams of a Sulfite Pulp Mill: A Preliminary Biorefining Approach

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Received 12 May 2015; Accepted 21 June 2015

Academic Editor: Ghadir A. El-Chaghaby

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The evolution of lignin, five- and six-carbon sugars, and other decomposition products derived from hemicelluloses and cellulose was monitored in a sulfite pulp mill. The wastewater streams were characterized and the mass balances throughout digestion and total chlorine free bleaching stages were determined. Summative analysis in conjunction with pulp parameters highlights some process guidelines and valorization alternatives towards the transformation of the traditional factory into a lignocellulosic biorefinery. The results showed a good separation of cellulose (99.64%) during wood digestion, with 87.23% of hemicellulose and 98.47% lignin dissolved into the waste streams. The following steps should be carried out to increase the sugar content into the waste streams: (i) optimization of the digestion conditions increasing hemicellulose depolymerization; (ii) improvement of the ozonation and peroxide bleaching stages, avoiding deconstruction of the cellulose chains but maintaining impurity removal; (iii) fractionation of the waste water streams, separating sugars from the rest of toxic inhibitors for 2nd generation biofuel production. A total of 0.173 L of second-generation ethanol can be obtained in the spent liquor per gram of dry wood. The proposed methodology can be usefully incorporated into other related industrial sectors.

1. Introduction

Mixed C5 and C6 hemicellulose sugar platforms serve as feedstock for fermentation producing biofuels such as ethanol or butanol, biopolymers such as polyhydroxybutyrate (PHB), or polybutylene succinate (PBS), and chemicals such as lactic acid, succinic acid, or itaconic or glutamic acids [1]. In Europe, primary energy consumption is dominated by the presence of petroleum products mostly imported from abroad. There are many concerns around the high degree of energy dependence [2]. Among the valorization alternatives described above, this work is based on bioethanol production from the pulp and paper industry, in order to be included in the transportation sector.

The pulp and paper industry is being reconsidered as an important source of hemicellulose carbohydrates. Traditionally, pulping manufacturing was focused on cellulose

extraction by chemical, mechanical or semichemical processes. Among the chemical processes, kraft is the most commonly used. However, other processes such as soda-anthraquinone (soda-AQ); ethanol-water pulping (organosolv); acid sulfite and bisulfite pulping; sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL); or SO₂-ethanol-water process (SEW) can also be used [3–10]. Sulfite pulping is becoming popular because of the growing demand of high purity dissolving pulp for textile fiber production. An advantage of sulfite pulping is regarding high separation efficiency of cellulose. While dissolving cellulose is manufactured, hemicellulose and lignin are also generated and partially reused. Conversion of these waste streams is becoming a clear priority within the biorefinery concept.

Nowadays, there are many efforts from the pulp and paper industries focused on sugar-rich resource valorization into energy and a wide variety of products. Several approaches

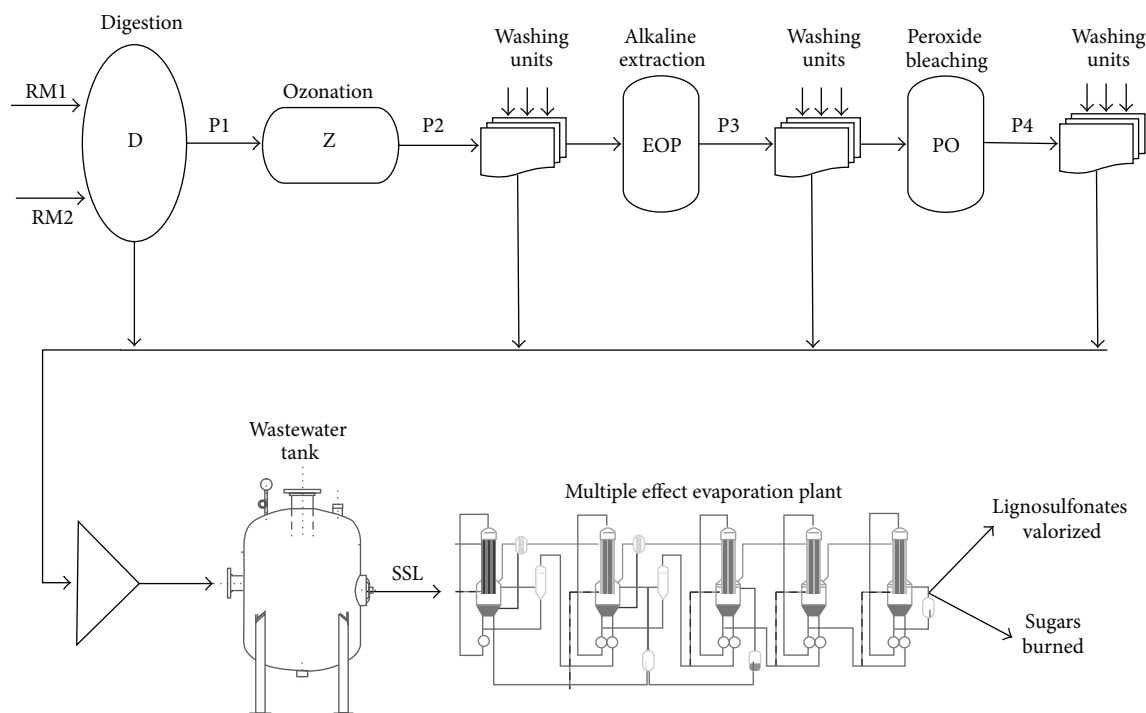


FIGURE 1: Raw materials, products, and by-products analyzed in this work in the acid sulfite process.

tracing pathways and guidelines towards the conversion of pulping factories into lignocellulosic biorefineries (LCBR) can be found in the literature for kraft pulping [11–14], soda-AQ [15, 16], organosolv [17–19], or SEW process [9, 10]. Nevertheless, only a few contributions have been studied in the case of sulfite pulping [20, 21]. The investment activity in this field reveals the importance of transforming traditional pulping factories into integrated LCBR, increasing the profit margin in the existing pulp mills. Due to the complexity of the lignocellulosic biomass (LCB), many efforts are being carried out in fractionation processes. In this sense, the first step was a deep control of the main resources throughout a total mass balance of the LCB. The mass balance provides a complete description based on lignin and carbohydrate content (hemicellulose and cellulose) of the materials [9, 22]. The use of total mass balances in a whole process can point out the main resources for valorization options. In addition, the study of digestion and bleaching allows the establishment of future actions towards process improvements. One of the methodologies to get the total mass balance in these kinds of samples is the summative analysis of the carbohydrates disclosure into their derivatives together with lignin, extractives, and ash contribution [22–24]. One advantage of this methodology is the possibility of the delignification and breakdown of the polysaccharides into individual sugars and other decomposition products, giving some information about possible inhibitors in future fermentation processes. This methodology was previously reported with purposes related to the characterization of bagasse and bamboo [23], different wood species [22–27], or pulps [28–32]. More recently, spent liquors provided from SEW were also characterized by summative analysis methodologies, tracing mass

balances for the residue bioconversion towards butanol, ethanol, and acetone/isopropanol [9, 10].

This work contemplates the study of the summative analysis in a sulfite pulp mill, monitoring the three main wood macrocomponents—cellulose, hemicellulose, and lignin—by measuring not only the raw material but also the residues and products throughout the process. In a second step, bioethanol potentials of the sugar-rich residue were also determined. This research constitutes a novelty in an industrial sulfite process towards the conversion of this factory into a modern LCBR. In addition, thanks to the compositional analysis together with the physic-chemical pulp properties (viscosity and micro kappa were also measured) the effects of digestion and bleaching steps were also investigated. The proposed methodology can be usefully extrapolated in not only sulfite or kraft mills but also other factories working with LCB.

2. Materials and Methods

2.1. Materials and Industrial Process Description. Figure 1 shows the industrial process and all of the materials collected in the pulp mill. The acid sulfite process is based on the extraction of cellulose by the attack of an acidic aqueous solution under acidic conditions (pH of 1.35 ± 0.15) in the presence of excess free SO_2 [2]. Delignification occurs inside the digester (see “D” unit in Figure 1) where the lignin is sulfonated by HSO_3^- forming lignosulfonates. Lignosulfonates together with high amounts of depolymerized hemicelluloses are dissolved into the so-called spent sulfite liquor (SSL) obtained at the end of the digestion stage. After digestion, the next step is bleaching (see “Z/EOP/PO” bleaching sequence in Figure 1). With the purpose of purifying the cellulose,

TABLE 1: Analytical procedures used in this work.

Parameter	Samples	Equipment	Standard/source
Samples conditioning		Mill, sieve, and climate chamber	TAPPI T257 cm-02 [33]
Acetone extractives	Wood and pulp	Soxhlet apparatus	TAPPI T204 cm-97 [33]
Ashes at 525°C		Muffle furnace	TAPPI T211 om-02 [33]
Cellulose		Analytical balance	Seifert [34]
Holocellulose	Wood	Analytical balance	Wise [35]
Lignin		UV-Vis	TAPPI T222 om-22 [33]
Micro kappa		Titration	TAPPI UM 246 [36]
Intrinsic viscosity	Pulp	Titration	ISO 5351:2010 [37]
Alfa-cellulose		Titration	TAPPI T203 cm-99 [33]
Glucan			
Xylan			
Arabinan	Wood, pulp, and SSL	(1) Hydrolysis	(1) TAPPI T249 cm-00 [33] (wood and pulp samples)
Galactan		(2) HPLC-RI	(2) Llano et al. [38] (wood, pulp, and SSL samples)
Mannan			
Acetyl			
Lignosulfonates	SSL	UV-Vis	UNE EN 16109 [39]

a total chlorine free (TCF) bleaching process is used in the factory. Ozone (Z), sodium hydroxide as the extracting agent together with oxygen and hydrogen peroxide (EOP), and hydrogen peroxide as the bleaching agent in the presence of oxygen (PO) are the stages followed in the pulp mill and studied in this work.

Wood, SSL, and pulp industrial samples were collected throughout the process as can be seen in Figure 1. *Eucalyptus globulus* timber is used as feedstock in this factory. On the other hand, SSL and industrial dissolving pulp samples were collected and analyzed in the process. A total of four delignification-grade pulps were analyzed starting with the crude pulp (P1) after the digestion stage and continuing with the bleaching stages after ozonation (P2); alkaline-extraction (P3); and peroxide oxygen bleaching (P4).

2.2. Analysis of Wood, Pulp and SSL. A summary of the characterization methods applied in this work is shown in Table 1. Wood and pulp samples were conditioned and prepared according to TAPPI T257 cm-02 [33]. Samples were air-dried to constant moisture to the nearest 10% w/w, milled, passed through 40-mesh sieve, and extracted with acetone in a Soxhlet apparatus in order to remove the extractives, according to T204 cm-97 standard [33]. Wood and pulp free-extractive samples were taken for the rest of the analysis. Ashes at 525°C were analyzed by TAPPI T211om-02 standard [33]. Acid-insoluble and soluble lignin were determined in wood samples by using TAPPI T222 om-02 method [33]. Cellulose content was determined using the Seifert procedure boiling a mixture of acetylacetone-dioxane-hydrochloric acid [34]. Holocellulose, which represents the total carbohydrate content (a sum of cellulose and hemicelluloses), was measured by means of the Wise chlorite technique reported recently by Haykiri-Acma et al. [35]. The lignin content (% on weight) in pulp was calculated by multiplying the kappa number by

0.17 [32]. Considering that the standard kappa number determination cannot be applied to pulp with kappa below five [41], micro kappa described in TAPPI UM 246 standard [36] was determined. To study the degradation of carbohydrate chains during the bleaching steps, intrinsic viscosity in crude, partially bleached, and bleached pulps was determined by means of the standard ISO 5351:2010 [37]. Alfa-cellulose was also measured in pulp samples using TAPPI standard T203 cm-99 [33].

SSL samples were studied in terms of lignosulfonates, sugars, and other decomposition products. The carbohydrate composition of wood, pulp, and SSL was conducted using HPLC/RID with the methodology published by Llano et al. [38]. Lignosulfonates were analyzed by UV-Vis spectroscopy, according to the UNE EN 16109 standard [39].

2.3. Hydrolysis Procedure, Summative Analysis Calculations, and Biofuels Potentials. Polymeric sugars contained in the cell wall of wood carbohydrates need to be broken down. The $\beta(1 \rightarrow 4)$ glycosidic linkages of the wood polymers are cleaved with the acid hydrolysis method described in TAPPI T249 cm-00 [33]. This method involves a two-step acid hydrolysis: (i) primary hydrolysis uses a strong acid at low temperature to convert the polysaccharides to oligomers, (ii) followed by the dilution to a weak acid at high temperatures to complete the conversion to monomeric sugars. First, free-extractive moisture-controlled samples were weighed at 0.35 ± 0.01 g into flask tubes. Then, 3 mL of 72% w/w H_2SO_4 was added into the glass test tubes, occasionally stirred in a vortex and maintained 1 h at 30°C into a thermostatic bath. The secondary hydrolysis was carried out at 120°C for 1 h after dilution to 4% by transferring hydrolyzates to Duran bottles and adding 84 mL of deionized water (Duran bottles must be hermetically closed). Afterwards, samples were cooled and a representative aliquot of 10 mL was transferred to a beaker.

TABLE 2: Stoichiometric factors used to calculate the percentage of theoretical homopolymer.

Hydrolyzed constituents	Homopolymer	Carbohydrate contribution	Conversion factor ^a	Hydrolysis factor ^b g.sugar/g.polymer	Ethanol factor ^c g.EtOH/g.monomer
Glucose	Glucan	Cellulose	162/180	1.11 ^b	0.511
HMF	Glucan	Cellulose	162/126	—	—
Levulinic acid	Glucan	Cellulose	162/116	—	—
Cellobiose	Glucan	Cellulose	324/342	—	—
Xylose	Xylan	Hemicellulose	132/150	1.136	0.511
Furfural	Xylan	Hemicellulose	132/96	—	—
Formic acid	Xylan	Hemicellulose	132/46	—	—
Arabinose	Arabinan	Hemicellulose	132/150	1.136	0.511
Galactose	Galactan	Hemicellulose	162/180	1.11	0.511
Mannose	Mannan	Hemicellulose	162/180	1.11	0.511
Acetic acid	Acetyl	Hemicellulose	43/60	—	—

^aStoichiometric factor used to calculate the percentage of theoretical homopolymer [22].

^bHydrolysis stoichiometric factor of carbohydrate polymers into free sugars [40].

^cEthanol stoichiometric factor describing the mass fraction of sugar monomer converted to ethanol [40].

Several drops of bromophenol blue indicator were taken and gradually neutralized adding 0.04 N Ba(OH)₂ alkaline solution to the aliquot until the solution changes from yellow to blue-violet. Then samples were centrifuged and 0.22 μm filtered and injected in the HPLC.

Each monomer can be reported in the summative analysis as its pure theoretical homopolymer [24]. The weight of each constituent, determined quantitatively after the hydrolysis, has to be multiplied by a factor to calculate its contribution to the original wood component (as a theoretical homopolymer). Calculations were made by using the theoretical stoichiometric factors obtained in the literature [22–24]. These factors consist of molecular mass of anhydrous unit divided by molecular mass of the isolated substance. Table 2 shows all of the conversion factors used in this work. Each homopolymer was calculated considering not only the monosaccharides but also the degraded-compounds derived from carbohydrates; for example, cellulose is the sum of cellobiose, glucose, HMF (5-hydroxymethyl-2-furfuraldehyde), and levulinic acid multiplied by their stoichiometric factors. The individual contribution of carbohydrate-derived compounds to the final cellulose or hemicellulose content depends on the chemical structure of the macromolecules forming the cell wall. In this work, all the glucose is assumed to generate from the cellulose [24]. Simultaneously, it was also assumed that formic acid is an inhibitor mostly produced from pentose sugars, being the formation of formic from hexoses negligible compared to the levulinic acid formation [42]. Acetic acid was considered a coproduct formed at the same time as monosaccharides by degradation of the acetyl groups located on the hemicellulose [43].

The macrocomponent calculations from their homopolymers are given by (1). Finally the total mass closure is calculated according to (1). In addition, ethanol potentials were calculated multiplying grams of each monomer by their corresponding stoichiometric factors (see Table 2). Such factors

describe the mass fraction of sugar monomers converted to ethanol [40]:

$$\begin{aligned}
 &\text{Total Carbohydrate Content} \\
 &= \text{Cellulose} + \text{Hemicellulose}, \\
 &\text{Hemicellulose} \\
 &= \text{Xylan} + \text{Arabinan} + \text{Galactan} + \text{Mannan} \\
 &\quad + \text{Acetyl}, \tag{1} \\
 &\text{Cellulose} = \text{Glucan}, \\
 &\text{Total Mass Closure} \\
 &= \text{Lignin} + \text{Total Carbohydrates} + \text{Extractives} \\
 &\quad + \text{Ash}.
 \end{aligned}$$

3. Results

3.1. Total Composition of the Lignocellulosic Samples. The results of the total content per sample are shown in Table 3, including the major components, ash, and extractives. The results represent the total weight percentage content of the industrial samples collected in the pulp mill. The total mass closure was near 100% in spite of the fact that some minority compounds were not analyzed such as low molecular phenolic compounds derived from lignin or aldonic and uronic acids derived from cellulose and hemicellulose.

The comparison of traditional characterization using gravimetric and titration methods and the carbohydrate analysis derived from the summative analysis calculations is displayed in Table 3. Traditional cellulose methods include alfa-cellulose in pulp [33] and Seifert for cellulose in wood [34]. Traditional hemicellulose in wood is calculated as the difference between holocellulose [35] and Seifert cellulose [34].

TABLE 3: Total weight content of industrial samples.

Total mass closure	<i>E. globulus</i> (% w/w)	SSL (% w/w)	P1 (% w/w)	P2 (% w/w)	P3 (% w/w)	P4 (% w/w)
Cellulose-HPLC	42.25	5.67	89	87.3	89.9	91.3
Cellulose	46.00	—	91.34	91.16	92.36	92.28
Hemicellulose-HPLC	24.92	30.42	6.2	5.1	2.2	2.1
Hemicellulose	31.55	—	—	—	—	—
Lignin	26.98	42.99*	0.80	0.40	0.40	0.10
Ash	0.35	12.1	0.28	0.26	0.24	0.18
Extractives	1.5	—	0.30	0.20	0.20	0.20
TOTAL	96	91.18	96.58	93.26	92.94	93.88

*Lignin in SSL is represented by the lignosulfonate content, formed by lignin sulfonation.

Cellulose-HPLC and hemicellulose-HPLC of wood and pulp samples were obtained stoichiometrically, after acid hydrolysis of carbohydrates and HPLC sugars quantification. Otherwise, SSL sugars were measured directly in the HPLC, avoiding the hydrolysis step.

Cellulose obtained by traditional methods and cellulose-HPLC in *Eucalyptus globulus* samples present values of 42.25% and 46%, respectively. The Seifert method entails higher experimental errors because of the wood digestion at high temperatures where some projections can be formed if the analysis is not carried out carefully. In pulp samples, the cellulose showed higher values by means of the traditional method. Alfa-cellulose corresponds to the insoluble fraction produced after the digestion of pulp at 25°C using 17.5% NaOH. Theoretically beta and gamma cellulose with a lower degree of polymerization are excluded, but considering the results of Table 3, there are chains with similar molecular weights that are also being quantified. Regarding the results of hemicellulose, the hemicellulose-HPLC is lower than hemicellulose calculated by traditional methods in wood 24.92% and 31.55%, respectively. This behavior could be explained by the assumption that the glucose content is only considered to form part of the cellulose fraction. In addition, gravimetric mistakes of Seifert and holocellulose methods are overlapping, giving more errors in comparison with the chromatographic method. An alternative to the study of hemicelluloses in pulp samples can be the pentosan determination with the T223 cm-01 procedure [33]; however, pentosan analysis was not performed in this work because it only contemplates the C5 sugars.

The results of the total carbohydrate content (TCC) disclosure appear in Table 4. TCC of 67.18% and 26.98% of lignin was obtained in *Eucalyptus globulus* hardwood samples. Besides, the replicates checked showed average values of 42.25% cellulose and 77.55% holocellulose. Results of lignin varying from 23% to 27% and cellulose from 45 to 54% of *Eucalyptus globulus* timber were found in the literature [26, 27]. Such ranges are in accordance with the results obtained in this work. The total content of xylan was 13.27% in wood samples, representing more than 50% of the total hemicellulose content. This is because hardwood, in contrast to coniferous softwood with a higher portion of hexosans than pentosans, is composed mainly of pentoses where xylose is the major monosaccharide [11, 44–46]. TCC is much higher in pulp samples in comparison with the *Eucalyptus globulus* samples.

The difference is explained because little amounts of lignin and hemicellulose were found in pulp samples. Hemicellulose decreases from 6.2% to 2.1% and lignin from 0.8% to 0.1% (see Table 3). TCC in pulp samples decreases in the bleaching processes, as can be seen in Table 4, from values of 95.2% to values of 91.8–93.4%. This phenomenon can be explained by the fact that xylan drops from 5.3% to 1.5% despite the fact that cellulose increases from 89.0% to 91.3%.

Once the total carbohydrates were obtained, a theoretical quantity of bioethanol was calculated according to the stoichiometric factors explained in Section 2.3. Results from 0.215 to 0.684 L ethanol per kg of dry sample were obtained.

3.2. Dissolving Pulp Properties: Results and Discussion. Pulp properties and their evolution within the sulfite process are represented in Figures 2(a), 2(b), 2(c), and 2(d). Pulp transformation from crude pulp after digestion stage (P1) to final bleached pulp (P4) is graphed with error bars.

Pulp quality parameters are represented in Figures 2(a) and 2(d). Glucan and alfa-cellulose have similar trends, especially in the alkaline extraction process; however some differences can be found in the case of ozonation with a more noticeable decrease of glucan. Pulp impurities were plotted, respectively, in Figures 2(b) and 2(c). In this case, similar results were obtained. Lignin and hemicellulose content decreases as the process advances. These results showed that the most oxidative stage is the ozonation where the main losses of lignin are registered from 0.8% to 0.4%. Although delignification is the main function of this stage, there is also a depolymerization of hemicelluloses from 6.2% to 5.1% because of the high oxidation produced by ozone. In spite of the recalcitrant nature of cellulose with no losses of alfa-cellulose, there is also a little decrease of glucan from 88.8% up to 87.3% probably due to the degradation of beta and gamma cellulose. Such behavior is also reflected in the viscosity falling from 706.4 mL/g to 568.2 mL/g. Figure 2(d) shows the polymerization degree of cellulose chains playing an important role in the quality of the final pulp. As was expected, the viscosity diminished stage by stage from 706.4 mL/g (P1) after digestion up to 492.5 mL/g (P4) after PO bleaching.

The obtained results were compared with other quality pulps as a function of the process (chemical or thermomechanical), the feedstock (softwood or hardwood), and the

TABLE 4: Total carbohydrate content of the woody hydrolyzates.

	Wood	SSL	Sulfite dissolving pulps (% w/w)			
	(% w/w)	(% w/w)	P1	P2	P3	P4
GLUCAN	42.25	5.67	89.0	87.3	89.9	91.3
Glucose	44.99 ± 2.13	4.12 ± 1.48	95.0 ± 3.81	93.7 ± 3.27	96.7 ± 2.42	98.1 ± 2.52
HMF	0.1 ± 0.03	0.02 ± 0.009	0.3 ± 0.001	0.3 ± 0.05	0.3 ± 0.002	0.3 ± 0.00
Levulinic acid	0.14 ± 0.03	0.01 ± 0.009	0.2 ± 0.09	0.2 ± 0.01	0.2 ± 0.02	0.4 ± 0.00
Cellobiose	1.51 ± 1.29	2.04 ± 0.16	3.1 ± 1.78	2.5 ± 1.95	2.4 ± 1.26	2.2 ± 1.84
XYLAN	13.27	19.15	5.3	4.5	1.7	1.5
Xylose	14.27 ± 0.47	21.43 ± 8.80	2.9 ± 0.67	2.7 ± 0.66	2.0 ± 0.42	1.7 ± 0.75
Furfural	0.2 ± 0.19	0.15 ± 0.055	0.4 ± 0.004	0.8 ± 0.02	0.1 ± 0.003	0.2 ± 0.001
Formic	0.15 ± 0.05	0.03 ± 0.028	0.3 ± 0.18	ND	ND	ND
ARABINAN	0.52	2.46	0.3	0.3	0.2	0.2
Arabinose	0.59 ± 0.36	2.79 ± 1.71	0.3 ± 0.13	0.4 ± 0.16	0.2 ± 0.09	0.3 ± 0.16
GALACTAN	7.36	3.03	0.4	0.3	0.3	0.4
Galactose	8.18 ± 1.53	3.36 ± 1.52	0.4 ± 0.09	0.4 ± 0.06	0.3 ± 0.09	0.4 ± 0.26
MANNAN	1.00	1.28	ND	ND	ND	ND
Mannose	0.011	1.42 ± 0.50	ND	ND	ND	ND
ACETYL	2.78	4.51	0.2	ND	ND	ND
Acetic	3.87 ± 0.32	6.30 ± 1.70	0.3 ± 0.24	ND	ND	ND
TCC (%)	67.18	36.09	95.2	92.4	91.8	93.4
^a EtOH (L/Kg.dw)	0.467	0.231	0.684	0.665	0.662	0.672
^b EtOH (L/Kg.dw)	0.441	0.215	0.639	0.630	0.642	0.651

^aEtOH (L/Kg.dry sample) calculated from the homopolymers using hydrolysis and fermentation factors.

^bEtOH (L/Kg.dry sample) calculated from the monomers using fermentation factors.

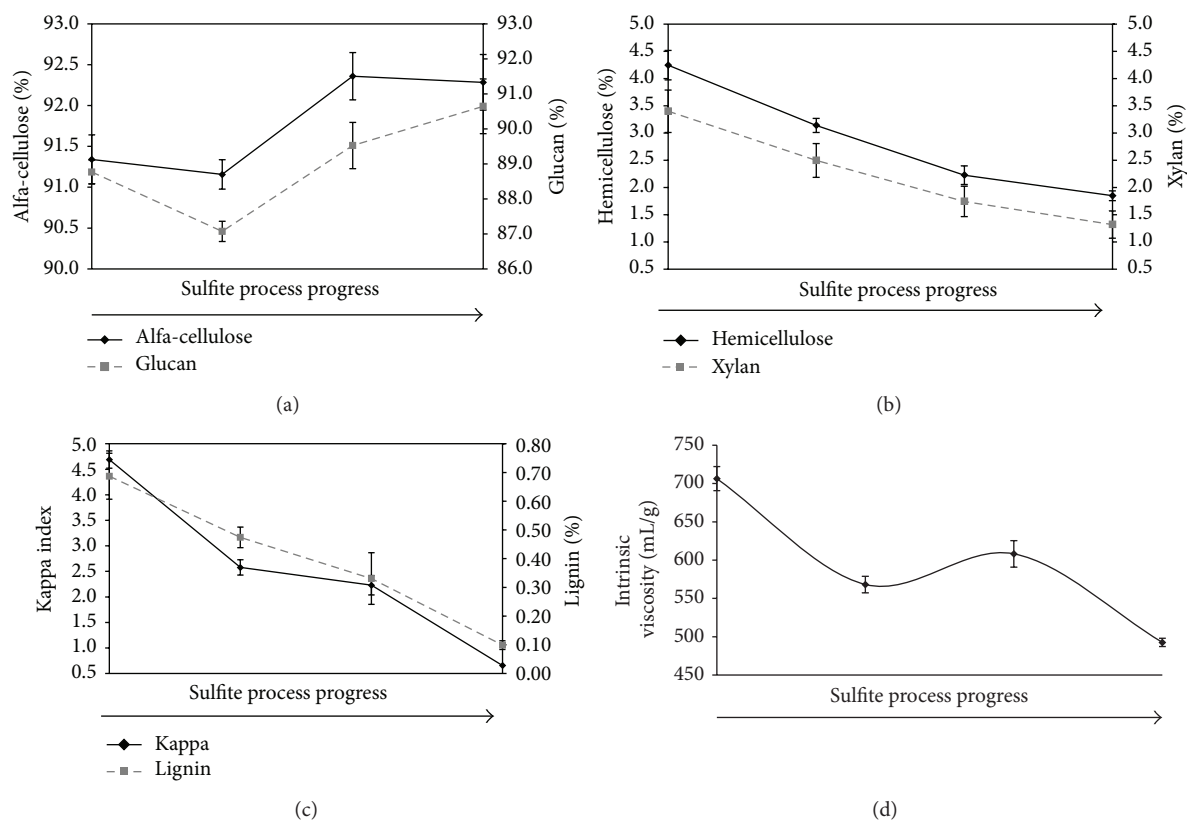


FIGURE 2: Evolution of wood macrocomponents in pulp along the sulfite mill: (a) glucan and alfa-cellulose; (b) hemicellulose and xylan; (c) kappa index and lignin; (d) viscosity in pulp.

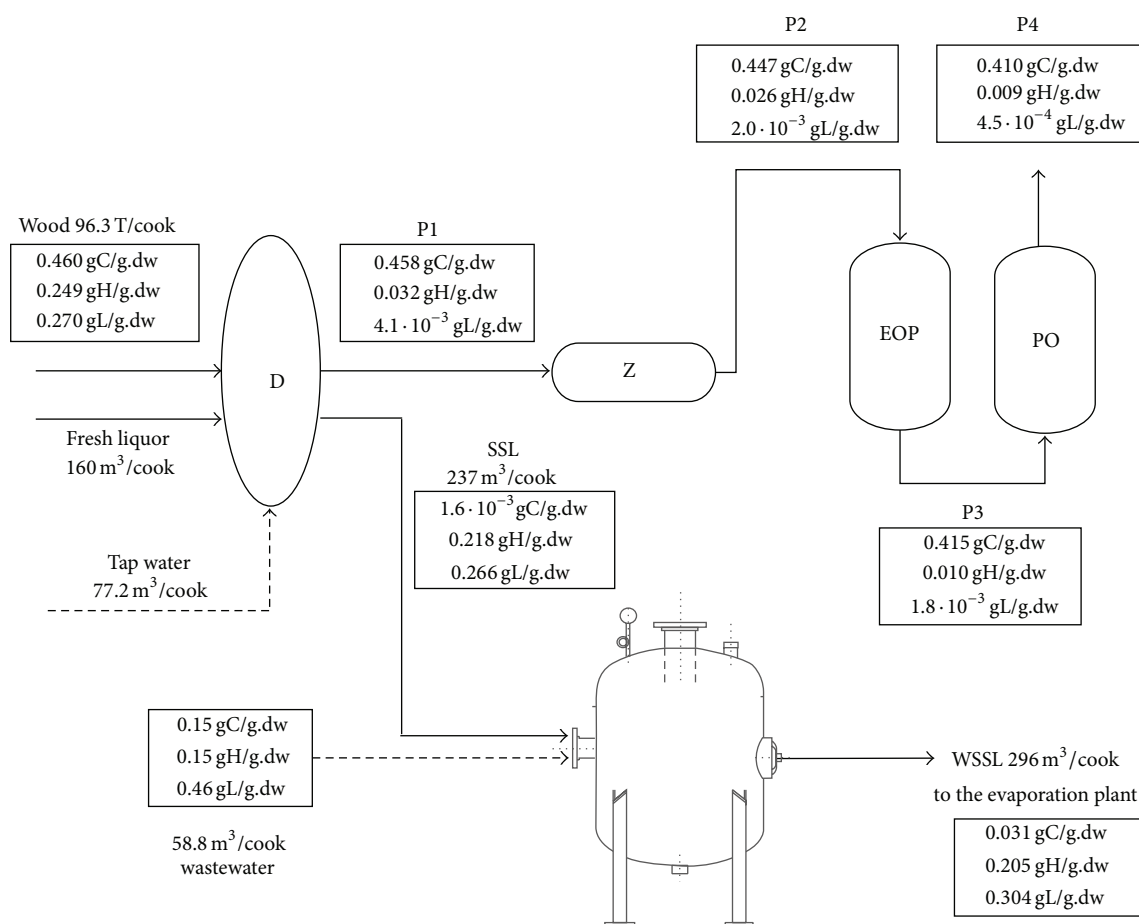


FIGURE 3: Mass balance results in the sulfite process. * Results expressed as gC/g.dw, gH/g.dw and gL/g.dw correspond to grams of cellulose, hemicellulose, and lignin per grams of dry wood, respectively.

final application (paper-grade or dissolving grade) [11, 28, 29, 47]. Results presenting major impurity removal are the more suitable for waste streams valorization towards biofuels and other value-added products. The worst pulp quality is the thermomechanical (TMP) pulp with a total carbohydrate content of 64.4% in comparison with chemical pulping processes with a total carbohydrate of 96.5% [30]. The TMP constituted low-purity (regarding the lignin content) and high-yield pulp. The difference between paper-grade and dissolving-grade pulp resides in the total glucan content that is lower in case of paper grade, obtaining values of 74.7% and 84.9% for hardwood and softwood bleached pulps [47] and 92.6% in the case of dissolving-grade pulps [29]. Consequently, the hemicellulose content is higher in paper-grade pulps than in high purity dissolving-grade pulps. In this work, total carbohydrate content in bleached pulp (P4) is 93.4% where 91.3% belongs to glucan with only 1.5% of xylan.

Based on the experimental results shown in Figure 2 it can be concluded that (i) ozonation stage (Z) produces the destruction of mainly lignin and also carbohydrates. Z focuses on delignification and therefore kappa is notably reduced. Nevertheless, glucan is considerably diminished during Z whereas this does not affect the alfa-cellulose. This is due to the fact that the ozone is very aggressive as a bleaching

agent (being less selective than chlorine derivatives) and attacks beta and gamma cellulose chains; (ii) hot alkaline extraction stage (EOP) focuses on hemicellulose solubilization, falling hemicelluloses from 5.1% to 2.2% and specifically xylan from 4.5% to 1.7%; (iii) peroxide bleaching stage (PO) attacks the chromophore groups and the pulp is definitely purified by removing lignin traces from 0.4% to 0.1% and other groups responsible for the color of the pulp; (iv) selectivity in PO and Z stages should be improved in order to avoid the breakdown of the cellulose chains; (v) results evidenced the importance of the wastewater streams valorization considering the high charge of organic compounds removed from the high-purity dissolving pulp along the sulfite process.

3.3. Mass Balance of the Industrial Process. The mass balance of the entire industrial process has been carried out taking into account the summative analysis. The complete characterization of the feedstock (*Eucalyptus globulus* timber), the inlet-outlet pulps, and the main residual stream (SSL) was required. Data of the three macrocomponents throughout the process, flow rates, digestions per day, wood moisture, or yields were considered. Some of the data are confidential to the factory and cannot be specifically displayed. Results appearing in Figure 3 have been correlated with the initial dry

wood in terms of grams of cellulose, hemicellulose, and lignin per grams of dry wood. The main discussion is described as follows:

- (i) A total content of 99.6% of cellulose provided from the feedstock goes to the main product, dissolving pulp, indicating the good performance of the digestion process. Only traces of wood cellulose are dissolved into the spent liquor. Thus, 0.032 g.hemicellulose/g.dry wood and $4.1 \cdot 10^{-3}$ g.lignin/g.dry wood were detected in the crude pulp (P1) which will be removed throughout subsequent stages.
- (ii) Based on the global mass balance and the conclusions of Section 3.2, some action lines can be made regarding Z and PO stages. A better use of the bleaching reagents and process conditions should be made in order to decrease the depolymerization degree but not to the detriment of delignification.
- (iii) The SSL generated after wood digestion is composed of 87.2% of the total hemicellulose in wood (0.218 g.H/g.dw) and 98.5% of the total lignin (0.266 g.L/g.dw). Hemicelluloses are hydrolyzed and dissolved as monosaccharides and other derivatives. Likewise, lignin reacts with sulfite, bisulfite ions, and sulfurous acid forming lignosulfonates. Based on these results SSL can be a perfect candidate for second-generation biofuel production.

The SSL is evaporated in the factory in order to reduce the water content. However, samples collected in this work were collected before the evaporation plant, at the tank outlet (see WSSL in Figure 3). Tap water is used at the end of the digestion stage to stop the hydrolysis and depolymerization reactions. In addition, wastewater streams provided from pulp washing containing cellulose, hemicellulose, and lignin are stored in the tank together with the SSL and sent to the evaporation plant as WSSL. Theoretical bioethanol potential of the WSSL was calculated based on the carbohydrates content (0.031 g.C/g.dw and 0.205 g.H/g.dw). The hydrolysis stoichiometric factors for hexoses and pentoses were, respectively, 1.11 g.C6-sugars/g.cellulose and 1.136 g.C5-sugars/g.hemicellulose; the fermentation stoichiometric factor for ethanol production is 0.511 g.EtOH/g.monosaccharide. Assuming the complete conversion of C5 and C6 sugars, the second-generation bioethanol potential of the WSSL is 0.173 L.EtOH/g.dw.

4. Conclusions

A full study of total mass balance throughout the entire sulfite pulping process in a pulp mill has been carried out, showing that the spent sulfite liquor is the most useful stream to be valorized due to the presence of lignosulfonates, sugars, and other minor compounds, giving a theoretical quantity of 0.173 L of bioethanol per gram of dry wood. Fractionation processes might be carried out to separate the value-added compounds, transforming this traditional pulp mill into a modern lignocellulosic biorefinery.

The characterization of the woody materials has been developed, comparing traditional methods with more novel methods based on the hydrolysis and individual characterization of the monomers. Acid hydrolysis is a useful method for the analysis of carbohydrate composition of wood and pulp samples. Using the TAPPI T249 cm-00 standard in combination with HPLC-RID technique can give complete information of the main components for valorization options in pulping processes.

Summative analysis results together with other parameters make studying every stage of the sulfite process possible. A favorable extraction of cellulose in the digester was carried out, with the presence of 99.6% of wood-cellulose in the crude pulp. On the other hand, 87.23% of hemicellulose and 98.47% of lignin are dissolved into the spent liquor.

Finally, some action lines to the existing process were indicated: (i) the digestion conditions should be optimized in order to increase the depolymerization of hemicelluloses in the spent liquor; (ii) ozonation and peroxide bleaching extraction processes should also be improved, avoiding the degradation and destruction of the cellulose chains and obtaining similar values of impurities; (iii) the spent liquor should be conveniently fractionated and detoxified, separating sugars from the rest of microbial inhibitors for second-generation biofuel production by microbial fermentation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors wish to express their sincere gratitude to the Sniace personnel and the financial support of the European Union by the BRIGIT “new tailor-made biopolymers produced from lignocellulosic sugars waste for highly demanding fire-resistant applications” research project <http://www.brigit-project.eu/>.

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