

ON THE RECOVERY OF HEMICELLULOSE BEFORE KRAFT PULPING

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To assess the feasibility of implementing hemicellulose recovery stages in kraft mills, *Eucalyptus globulus* wood samples were subjected to aqueous treatments with hot, compressed water (autohydrolysis processing) to achieve partial dissolution of xylan. Autohydrolyzed solids were subjected to kraft pulping under selected conditions to yield a pulp of low kappa number, and to an optimized TCF bleaching sequence made up of three stages (alkaline oxygen delignification, chelating, and pressurized hydrogen peroxide), with minimized additions of pulping and bleaching chemicals. The final product had a relatively low kappa number (1.4), 641 mL/g ISO intrinsic viscosity, and 86.4% brightness.

Keywords: Autohydrolysis; Biorefinery; *Eucalyptus globulus* wood; Hemicellulose; Kraft pulping

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INTRODUCTION

Important problems such as the depletion of fossil fuels, the expected increase in their future prices, the environmental concerns associated with their use (particularly those derived from the greenhouse effect), and uncertainties related to the security of supply are boosting the search for alternative, renewable raw materials whose manufacture would address these societal needs.

Lignocellulosic materials (LCM), including wood, are natural feedstocks potentially suitable for replacing fossil fuels as an alternative means. Utilization of LCM can be carried out by “fractionation” technologies, which intend the separation of LCM components with different properties into different streams and the further processing of these fractions for defined product applications. This concept is analogous to the one followed in petroleum refineries. Because of this, the integrated facilities in which LCM are processed to obtain a wide spectrum of products are called “biorefineries”. According to the International Energy Agency, biorefineries are intended to achieve sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, materials) and bioenergy (biofuels, power, and/or heat).

In the kraft process, the world’s leading pulping technology, the lignocellulosic feedstock is treated in alkaline media containing hydroxide, sulfide, and bisulfide ions (“white liquor”), causing the dissolution of lignin and part of the hemicelluloses. Pulping results in the production of both pulp and pulping liquor: the pulp (containing residual hemicelluloses and some lignin) displays good mechanical strength, while the pulping

liquor (“black liquor”) is further concentrated and burned, enabling the recovery of pulping chemicals. Because the overall energy balance of the process (including thermal energy and electricity generation) is favourable, the surplus electricity can be sold as clean energy. Depending on the type of wood employed in the process, tall oil (a fraction employed as an emulsifier and in the manufacture of adhesives, inks and rubbers, mainly made up of rosins, sterols, acids and alcohols) is obtained as a process byproduct.

In pulp and paper mills, LCM are treated to separate cellulose from the rest of the structural components, and additional value can be obtained from the surplus energy or tall oil. This conceptual framework fits in the biorefinery concept, providing a preliminary scheme for the further development of advanced biorefineries. In fact, the concept of producing cellulosic biofuel, bioproducts, and chemicals from lignocellulose has been around for over a century (Zhu 2011).

The concept of a biorefinery has been considered the key to unlocking biomass as a feedstock (Clark *et al.* 2009). Focusing on the replacement of fuels and chemicals currently derived from petroleum, it can be noted that in kraft mills, part of the hemicelluloses (which have a low specific combustion enthalpy) are burned, providing a limited added value, whereas extracting hemicelluloses before pulping may provide competitive advantages, as they can be used as substrates for the manufacture of multiple commercial products such as xylose and other hemicellulosic sugars, xylooligosaccharides, furans, ethanol, lactic acid, acetone, butanol, citric acid, propylene glycol, xilitol, formaldehyde, butanediol, propanediol, and cellulolytic enzymes (Towers *et al.* 2007; Gullón *et al.* 2011). However, hemicellulose extraction results in decreased feeding of saccharides to the kraft recovery boiler, which in turn may entail added costs associated with either reducing steam use in the mill or increasing steam production from other boilers on-site (Towers *et al.* 2007).

The extraction of hemicelluloses from wood chips prior to pulping for use as a biochemical feedstock is one of the research subjects included in the “Agenda 2020” program supported by the American Forest & Paper Association. Pulping hemicellulose-free substrates is not new, as it is performed at the industrial level in the prehydrolysis-kraft process for dissolving pulp manufacture (Patrick 1977). However, this technology is based on the use of steam under harsh operational conditions, which causes hemicellulose decomposition, making the hemicellulose-derived products unsuitable as substrates for the manufacture of transportation fuels.

Hemicelluloses can be extracted from wood under alkaline, near-neutral, mild acidic, or acidic conditions. Alkaline extraction and treatments with externally added acids (prehydrolysis) lead to polymeric materials and sugar-containing prehydrolyzates, respectively, entailing the consumption of chemicals for pH regulation and neutralization. Mild acidic conditions are achieved by treatments with hot, compressed water (also called autohydrolysis or hydrothermal processing), as organic acids are generated *in situ* (particularly by acetyl group hydrolysis), with no need of additional chemicals. Near-neutral conditions can be achieved when reaction media made up of wood and water are supplemented with solutions of various bases, buffers, or alkaline pulping streams.

Because the addition of chemicals other than water is not needed in autohydrolysis, this technology can be considered environmentally friendly (Garrote *et al.* 1999). Biorefinery schemes based on the selective hydrolysis of hemicelluloses by

autohydrolysis have been proposed (Yáñez *et al.* 2009; Gullón *et al.* 2011). In particular, coupling hemicellulose extraction and pulping stages has been considered in the literature for a variety of substrates including hardwoods, softwoods, and non-woody materials, and a number of delignification technologies, including the kraft method (Chirat *et al.* 2010; Mendes *et al.* 2009 and 2011; Colodette *et al.* 2011; Vila *et al.* 2011), as well as alkaline sulfite (Kordsachia *et al.* 2004; Al-Dajani and Tschirner 2010), soda-antraquinone (García *et al.* 2011a, b), alkaline sulfite anthraquinone methanol (Al Dajani and Tschirner 2010), ethanol (Garrote *et al.* 2003; Alfaro *et al.* 2010; Caparrós *et al.* 2007, 2008), and a number of other pulping technologies.

Focusing on the autohydrolysis-kraft processing of wood, two different aspects have to be balanced: On the one hand, autohydrolysis must ensure a substantial degree of hemicellulose solubilization to achieve concentrations of hemicellulose-derived saccharides high enough to make any further use profitable. On the other hand, harsh conditions lead to a number of undesired effects (particularly lower intrinsic fiber strength and inter-fiber bonding, resulting in poor pulp viscosity). The limited intrinsic fiber strength of pulps obtained by the prehydrolysis-kraft process has been considered a consequence of the higher level of local defects introduced into the fibers by the pretreatment (Santos *et al.* 2008), and in addition the cellulose molecular degradation (manifested in lower average degree of polymerization) caused by hydrothermal processing has been an object of interest (Sundqvist *et al.* 2006).

The present work provides an experimental assessment of the autohydrolysis-kraft processing of *Eucalyptus globulus* wood. Autohydrolysis was carried out under conditions of intermediate severity (leading to partial xylan removal), and pulping was conducted under conditions adapted to the particular characteristics of the autohydrolyzed substrates. For comparative purposes, kraft pulps were obtained using wood as a raw material. Bleaching was carried out using a three-stage Totally Chlorine Free (TCF) sequence, and the pulp properties were measured.

EXPERIMENTAL

Analysis of the Raw Material

Eucalyptus globulus wood chips were collected from a local pulp producer (ENCE, Pontevedra, Spain). Samples of the raw material were assayed for extractives (TAPPI T-264-om-88m method), moisture (TAPPI T-264-om-88m), ash (T-244-om-93), and quantitative acid hydrolysis with 72% w/w sulphuric acid (T-249-em-85). Liquors from quantitative acid hydrolysis were analyzed by HPLC for sugars (glucose, xylose, and arabinose) and acetic acid using a Refractive Index (RI) detector and a BioRad Aminex HPX-87H column, which was eluted with 0.003 M H₂SO₄ at a flow rate of 0.6 mL·min⁻¹.

The wood content of the polysaccharides (cellulose, xylan, and arabinan) and acetyl groups were calculated from HPLC data. The Klason lignin content of wood was measured from the solid residue obtained in the quantitative acid hydrolysis step after correction for ash.

Autohydrolysis Processing

Eucalyptus globulus wood and water were processed in a 6-vessel rotating L&W digester (which holds a dry wood load of 1200 g), kept at the target temperature for the desired time by immersion in a polyethylene bag with automatic temperature control, and cooled. Details on the operational conditions are shown below. Liquors were separated by filtration, and an aliquot was filtered through 0.45 μm membranes and used for direct HPLC determination of glucose, xylose, arabinose, acetic acid, hydroxymethylfurfural, and furfural using the same method specified above. A second aliquot was subjected to quantitative posthydrolysis with 4% w/w sulphuric acid at 121°C for 30 min., filtered through 0.45 μm membranes, and analyzed by HPLC. The increase in the concentration of sugars and acetic acid caused by posthydrolysis provided a measure of the oligomers and linked acetyl groups. A third aliquot was dried at 105°C to constant weight to determine the liquor content of non-volatile compounds (NVC).

Spent solids from autohydrolysis were washed with distilled water, air dried, and employed for solid yield determination (expressed as g spent solid recovered/100 g raw material, on dry basis). Aliquots of spent solids were dried and milled to a particle size less than 0.5 mm and analyzed using the same methods employed for wood analysis.

Wood chips (used as a reference material) and solids from autohydrolysis treatments were subjected to kraft pulping in the rotating digester cited above under conditions reported as optimal for each case. Pulp yield, kappa number, brightness, and intrinsic viscosity were measured using standard ISO methods (302:2004, 3688:1999, and 5351/1:2010, respectively).

TCF bleaching was performed according to an optimized O-Q-(PoP) TCF sequence (O, alkaline oxygen delignification; Q, chelating stage; PoP, pressurized hydrogen peroxide bleaching followed by an atmospheric stage, with no interstage washing). The operational conditions in each stage were fixed (according to the properties of the corresponding substrates) as indicated below.

Mechanical Properties of Pulps

Pulps were disintegrated (ISO 5263-1 method) and refined (ISO 5264-2 method). Laboratory sheets were prepared according to the ISO 5269-1 standard and assayed for tensile index, tear index, and burst index using the methods ISO 5270 1924-3, ISO 5270 1974, and ISO 5270 2758, respectively.

RESULTS AND DISCUSSION

Raw Material Composition and Autohydrolysis Processing

The raw material composition (expressed in g/100 g oven-dry wood) was as follows: cellulose, 45.0.; xylan, 17.5; arabinan, 1.20; acetyl groups, 3.27; Klason lignin, 27.8; extractives, 2.4; and ash, 0.24.

Several studies that have reported on hemicellulose extraction by water processing and further kraft pulping of autohydrolyzed solids have considered a wide range of experimental conditions. Even if the severities employed in the various studies are difficult to compare (owing to the different heating profiles and parameters used to

measure the harshness of treatments, such as the H-factor or the severity factor defined by Overend and Chornet (1987), the percentage of wood solubilization (or, alternatively, the percentage of xylan removal) achieved in autohydrolysis gives a valid basis for comparison. Mendes *et al.* (2009) performed the autohydrolysis under low severity conditions (150°C for 180 min.), solubilizing 12.5 to 13.1% of the *Eucalyptus globulus* wood. Liquor was subjected to posthydrolysis with 4% sulfuric acid to yield a fermentable xylose solution, and the solid from autohydrolysis was subjected to Elemental Chlorine Free (ECF) bleaching. Colodette *et al.* (2011) treated *Eucalyptus urograndis* with water at 165°C for 10 to 60 min., solubilizing 5 to 16.2% of the wood mass. The expected potential xylose concentration in the liquor (limited by a low xylan content of wood) was not considered high enough for the economical manufacture of ethanol, and the authors suggested other target applications for xylan-derived saccharides. On the other hand, pulps from autohydrolyzed solids were fully bleached using an ECF sequence. Vila *et al.* (2011) subjected *Eucalyptus globulus* wood to non-isothermal autohydrolysis at 196°C, solubilizing 25% of the original wood (achieving 80% recovery of xylan as soluble saccharides), and they employed the autohydrolyzed solids as a substrate for kraft pulping and further TCF bleaching. The resulting pulps showed reduced viscosities, in the target range for dissolving pulp applications.

Based on the above information, and aiming to perform the autohydrolysis of *Eucalyptus globulus* under conditions leading to significant xylan conversion into soluble saccharides while obtaining autohydrolyzed solids still suitable for kraft pulping, preliminary autohydrolysis experiments (data not shown) were carried out in order to identify the operational conditions leading to 18 to 19% wood solubilization (for which about 50% xylan removal was expected). The experimental information allowed the selection of the following operational conditions: hydromodule, 4.0; heating time, 90 min.; temperature, 165°C; and reaction time, 40 min. Under these conditions, 18.3% of the initial wood was dissolved in the treatments, leading to a liquor with the composition shown in Table 1.

Table 1. Composition of the Liquor from Autohydrolysis

Component	Concentration, g/L
Glucose	0.40
Xylose*	4.37
Arabinose	0.85
Glucooligosaccharides (as glucose)	1.18
Xylooligosaccharides (as xylose)*	18.3
Arabinosyl substituents of oligosaccharides (as arabinose)	0.00
Acetyl substituents of oligosaccharides (as acetic acid)	3.97
Formic acid	0.689
Acetic acid	1.77
Hydroxymethylfurfural	0.057

*Containing minor amounts of galactose and mannose (which are coeluted together with xylose in HPLC analysis)

Based on the cellulose and xylan contents of the wood, it can be concluded that more than 98% of the original cellulose was recovered in autohydrolyzed solids and that 48.5% of the initial xylan was converted into soluble xylooligosaccharides, xylose, or furfural. Acetic acid and acetyl groups in oligosaccharides accounted for about 46% of the stoichiometric amount. Autohydrolyzed solids contained 93% of the Klason lignin present in wood.

Pulping of Autohydrolyzed Solids and Bleaching of the Resulting Pulps

Even though the data from the literature concerning kraft pulping of *Eucalyptus* wood are difficult to compare (owing to differences in methodology and operational conditions, incomplete information, and differences in the target values selected for residual xylan and *kappa* number), the existing information reveals that autohydrolyzed solids and wood present a different behaviour when subjected to kraft pulping.

Beyond the obvious differences in overall pulp yield and residual xylan, some general ideas of practical importance can be summarized as follows (Vila *et al.* 2011; Mendes *et al.* 2009; Colodette *et al.* 2011):

- First, autohydrolyzed solids are more susceptible to delignification than raw wood (yielding pulps of lower *kappa* number under the same pulping conditions or yielding similar *kappa* numbers under milder conditions). Also, pulps obtained from autohydrolyzed wood present high susceptibility towards alkaline oxygen delignification and decreased pitch-related problems (owing to the partial removal of extractives in the autohydrolysis stages).
- On the other hand, intrinsic viscosity, which measures the degree of polymerization of polysaccharides and is commonly related to pulp strength (Carvalho *et al.* 2000), may drop when the autohydrolysis stage is carried out under harsh conditions. Increased pretreatment severities decreased both pulp beatability and paper properties. Pulp yields are decreased by the limited residual xylan in pulps, and pulps of low xylan content are expected to present poor technological properties such as fibre swelling, flexibility, and conformability.
- Among these effects, the viscosity drop caused by autohydrolysis has been identified as the main challenge to be addressed in the autohydrolysis-kraft delignification of *Eucalyptus* wood (Vila *et al.* 2011).

To assess the susceptibility of autohydrolyzed solids toward kraft pulping, the set of experiments indicated in Table 2 was carried out. Experiments were performed at 165°C under fixed conditions except for reaction time and active alkali (AA).

The sample of *Eucalyptus* wood was treated at 165°C for 50 min. in media containing 12.5 to 15.0% AA, yielding pulps with *kappa* numbers in the range of 22.3 to 15.9 at yields in the range of 59.6 to 55.1%. Autohydrolyzed solids were pulped in preliminary experiments at 165°C using various alkali charges (data not shown) in order to identify both a delignification time (40 min.) and the active alkali loading range (13.0 to 15.0) suitable for the purposes of this study. Operating under these conditions, the pulps were obtained at yields in the range of 54.8 to 51.0 g/100 g autohydrolyzed solids, or at “corrected yields” in the range of 44.8 to 41.7 g/100 g raw wood, with *kappa* numbers in the range of 25.4 to 10.3.

Table 2. Operational Conditions Employed in Kraft Pulping Experiments*

Pulping Substrate	Operational Conditions		Experimental Results				
	Reaction time, min	AA, %	Pulp yield, kg/100 kg substrate	Corrected yield, kg/100 kg wood	Rejects, %	kappa number	ISO intrinsic viscosity, mL/g
<i>E. globulus</i> wood (reference material)	50	12.5	59.6	59.6	12.3	22.3	1468
		13.0	58.0	58.0	7.3	19.8	1417
		13.5	57.3	57.3	6.9	18.9	1402
		14.0	55.9	55.9	4.0	17.1	1399
		14.5	55.2	55.2	4.5	16.2	1348
		15.0	55.1	55.1	3.0	15.9	1345
Autohydrolyzed solids	40	13.0	54.8	44.8	8.0	25.4	-
		13.3	54.0	44.1	5.0	22.0	1397
		13.6	52.1	42.6	1.5	13.5	1304
		14.0	51.9	42.4	1.5	13.2	1289
		15.0	51.0	41.7	0.8	10.3	1188

*Fixed variables: hydromodule 3.5, sulfidity 25%, temperature 165 °C, heating time 90 min

According to the data, both raw wood and autohydrolyzed solids can yield pulps with kappa numbers of about 16 and with intrinsic viscosities of about 1330 mL/g. For this purpose, both the shorter reaction time (50 min. for wood, 40 min. for autohydrolyzed solids) and the lower active alkali (14.5 to 15% for wood and about 13.5% for autohydrolyzed solids) confirmed the advantages of using mild cooking conditions when autohydrolyzed solids are used as a substrate for pulping. In comparison with reported data (Vila *et al.* 2011), the milder autohydrolysis conditions considered in this work enabled about 30% increase in intrinsic viscosity. Interestingly, pulps of limited kappa value (in the range of 11 to 12) could be obtained at good viscosities (slightly higher than 1200 mL/g). The experimental results are in the range reported by Mendes *et al.* (2009) for kraft pulps of *Eucalyptus globulus* wood autohydrolyzed under milder conditions (1268 mL/g at a kappa number of 13.1).

The bleachability of autohydrolyzed solids was assessed using a selected sample (with 11.3 kappa number and 1217 mL/g intrinsic viscosity), which was obtained at a yield of 50.5 kg/100 kg autohydrolyzed solids and considered favourable owing to its balance between low lignin content and still good intrinsic viscosity. Bleaching was performed using an optimized O-Q-(PoP) TCF sequence, which was expected to be less demanding in terms of viscosity than the OOQ(PoP) sequence employed in an earlier work (Vila *et al.* 2011). Tables 3 and 4 show the operational conditions used in the various bleaching stages and the corresponding experimental results.

Based on data from the literature and on results achieved in previous experiments (data not shown), the first O-stage was performed under the conditions indicated in Table 3 (1.5% NaOH at 6 kg/cm² of partial O₂ pressure), obtaining a pulp with a kappa number of 3.6, intrinsic viscosity of 962 mL/g, and 62.7% brightness. In comparison, when a commercial, unbleached kraft pulp obtained from raw wood (kappa number, 16.3; intrinsic viscosity, 1365 mL/g) was subjected to an O-stage under the same conditions, the resulting product showed the following properties: kappa number, 11.2; intrinsic viscosity, 1234 mL/g; and brightness, 52.9%.

Table 3. Operational Conditions Employed in the TCF Bleaching of Pulps Obtained from Autohydrolyzed Solids

Operational Conditions	Bleaching Stage		
	O	Q	(PoP)
Consistency %	10	10	10
Temperature °C	98	85	105
Time min.	60	60	120*
DTPA %	-	0.3	-
NaOH %	1.5	-	1.5
H ₂ O ₂ %	-	-	2.0
MgSO ₄ %	0.5	-	0.1
Na ₂ Si ₂ O ₃ %	-	-	0.5
O ₂ pressure kg/cm ²	6	-	6
pH	-	5-6	-
*Followed by an atmospheric stage at 98 °C for 210 min with no interstage washing			

Table 4. Results Achieved in the Bleaching of the Pulp Obtained from Autohydrolyzed Solids

Pulp Properties	After the O-stage	After the Q-stage	After the (PoP) stage
<i>kappa</i> number	3.6	3.5	1.4
ISO intrinsic viscosity, mL/g	962	945	641
Brightness, %	62.7	63.7	86.4
pH	10.4	5.6	10.2
Residual H ₂ O ₂ , g/L	-	-	0

The data confirmed the high susceptibility of the product obtained by autohydrolysis pulping to delignification by oxygen treatments: typical operational conditions decreased the kappa number by 68% (in comparison with 31% kappa reduction for pulps obtained from raw wood), yielding a product of remarkably low lignin content and good brightness. Conversely, the O-stage caused 21% intrinsic viscosity loss, in comparison to about 10% intrinsic viscosity drop for non-autohydrolyzed substrates. It can be noted that the differences between the viscosities determined for oxygen-delignified pulps from raw wood and for autohydrolyzed solids (1234 and 962 mL/g, respectively) cannot be compared directly, owing to the different kappa numbers (11.2 and 3.6). As expected, the Q-stage resulted in minor effects (less than 2% intrinsic viscosity loss and about 1% brightness gain). The final PoP stage, performed using a limited peroxide charge (2%), boosted brightness up to 86.4%, causing limited effects in kappa number (which dropped just 0.1 units) but reducing intrinsic viscosity by 32%. The percentage of intrinsic viscosity loss was similar to that achieved when a commercial pulp obtained from raw wood after an O-O-Q sequence was subjected to a PoP stage with 3.3% peroxide charge, which resulted in a product with following properties: kappa number, 5.6; intrinsic viscosity, 721 mL/g; and brightness, 88.4%. In summary, in comparison with commercial pulps obtained from raw wood, the autohydrolysis-kraft pulping-TCF bleaching method enabled the retention of pulping and bleaching chemicals and led to pulps of lower kappa number (1.4 in comparison with 5.6) and reasonable intrinsic viscosity and brightness (641 mL/g and 86.4%, in comparison with 721 mL/g and 88.4%, respectively).

Mechanical Properties

Table 5 shows the data obtained for the bleached pulp obtained from autohydrolyzed wood. The results are poor in comparison with the data reported for native wood, and confirm the findings reported in related studies regarding the damage in physical strength caused by hydrothermal processing (Colodette *et al.* 2010, Caparrós *et al.* 2008, García *et al.* 2011b). On the basis of the experimental results, it can be inferred that the pulps are not directly suitable for applications requiring strong physical properties, even if defined thresholds could be reached just by supplementation with the necessary proportions of high-strength pulps. However, the properties of pulps obtained by the autohydrolysis-pulping-TCF bleaching scheme would make them potentially suitable for specific applications not demanding high strength (for example, tissue), as well as for manufacturing higher added-value products such as dissolving pulps or microcrystalline cellulose.

Table 5. Mechanical Properties of the Bleached Pulp Produced from Autohydrolyzed Solids

PFI rev.	2000	3000	4000
Burst Index, kPa.m ² /g	0.84	1.20	1.59
Tensile Index, N.m/g	15.3	21.3	28.1
Tear Index, mN m ² /g	3.30	3.80	4.40

CONCLUSIONS

1. Hemicellulose recovery prior to kraft pulping was assessed by subjecting *Eucalyptus globulus* wood samples to autohydrolysis processing under mild conditions (hydromodule, 4.0; heating time, 90 min.; temperature, 165°C; reaction time, 40 min.). Processing resulted in the dissolution of about 50% of the original xylan.
2. Autohydrolyzed solids were subjected to kraft pulping under low severity conditions. A selected pulp with good balance between kappa number (11.3) and intrinsic viscosity (1217 mL/g) was bleached using an optimized O-Q-(PoP) sequence. Autohydrolyzed solids were highly susceptible to oxygen delignification, which resulted in a pulp with 3.6 kappa number, 962 mL/g intrinsic viscosity, and 62.7% brightness.
3. A further Q-stage resulted in minor effects (less than 2% viscosity loss and about 1% brightness gain); however, the final PoP stage increased brightness up to 86.4% and reduced intrinsic viscosity to 641 mL/g. Both parameters were close to the values (721 mL/g intrinsic viscosity and 88.4% brightness) determined for a commercial pulp used as a reference.

ACKNOWLEDGMENTS

The authors are grateful to “Xunta de Galicia” for supporting this study, in the framework of the research Project “Hemicellulosic bioethanol: Compatibility with the kraft process” (reference 09REM003383PR). This Project was funded in part by the FEDER Program of the European Union.

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Article submitted: March 13, 2012; Peer review completed: May 28, 2012; Revised version received: July 9, 2012; Second revised version accepted: July 18, 2012; Published: July 20, 2012.