MULTISTAGE ORGANOSOLV PULPING: A METHOD FOR OBTAINING PULPS WITH LOW HEMICELLULOSE CONTENTS

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Two-stage treatments of *Eucalyptus globulus* wood were carried out in HCl–acetic acid–water media in order to obtain high-purity cellulose pulps. The effects of selected operational variables affecting the first pulping stage on the yield and composition of delignified solids were determined. A pulp selected from this study was used as substrate for a further pulping stage, which was carried out either at the normal boiling temperature or at 130 °C under a variety of conditions. This method was found to be particularly suitable for obtaining pulps with low hemicellulose contents.

Keywords: Acetic acid pulping; Acetosolv process; *Eucalyptus globulus* wood; Organosolv pulping; Cellulose; Acid hydrolysis.

Organosolv pulping based on the utilization of organic solvents as pulping media[1–4], show interesting features including: (i) low environmental impact, (ii) reduced capital investment for small-size plants and production of profitable byproducts, (iii) high delignification selectivity, (iv) capability of producing easily bleachable pulps, and (v) absence of odoriferous emissions.

Acetic acid has received particular attention among the variety of organic solvents considered for delignification. In the Acetocell process, aqueous acetic acid solutions are employed for delignification in the absence of catalysts, whereas in the Acetosolv and Formacell processes, HCl and formic acid, respectively, are used as catalysts[4–8].

Hardwoods and softwoods have been successfully pulped by the Acetosolv method[5,9–11]. Data dealing with the optimization of Acetosolv pulping of *Eucalyptus globulus* wood as well as on the reaction mechanism and kinetics have been reported[12–15]. In this field, a possibility of implementing sequential treatments for enhancing removal of both lignin and hemicelluloses remains to be assessed. It can be noted that this second stage can be easily implemented in a continuous process, because small effects caused in pulps would allow direct recycling or reutilization of the li-

quors. Multistage operation has been previously reported for other organo-solv processes with formic acid[16] or ethanol[17].

This work deals with the evaluation of possible improvements derived from coupling two Acetosolv pulping stages. The first one was carried out at low liquor-to-wood ratios (4 or 7 g/g), and was optimized with respect to both catalyst (HCl) concentration and reaction time. The second stage was carried out with the best pulp produced in the previous study, which was subjected to harsh operational conditions in order to achieve pulps with decreased hemicellulose contents.

EXPERIMENTAL

Eucalyptus globulus wood chips were provided by ENCE (Pontevedra, Spain). Wood chips were screened to separate a particle fraction below 2 mm, homogenized in a single lot to avoid compositional differences and stored. Pulping assays were carried out in glass reactors with temperature control or in autoclave under the operational conditions described in text.

Analytical characterization of raw material and pulp. Analytical assays were performed using the following methods: moisture, ISO 638:1978 method; quantitative acid hydrolysis, TAPPI T13m method; Klason lignin, by gravimetric determination of the residue from the TAPPI T13m assay; cellulose (as glucan), by HPLC determination of glucose contained in hydrolysates from the TAPPI T13m assay using an Interaction Ion column with H_2SO_4 as eluent and RI detection[18], hemicelluloses, by HPLC determination of the non-glucose sugars (xylose and arabinose) contained in hydrolysates from the TAPPI T13m assay[18]; acetyl groups, by HPLC determination of acetic acid in the same hydrolysates; furaldehyde and sugars in pulping liquors, by direct HPLC analysis of the hydrophilic phase obtained after water addition and lignin precipitation (using the same method as for sugar analysis but with UV detection).

RESULTS AND DISCUSSION

Acetosolv Pulping at Low Liquor-to-Wood Ratios

Two sets of experiments (9 assays each) were carried out to assess the possibility of operating at high solid concentrations in HCl–acetic acid–water media, an important point not considered in literature. In order to improve the extent and selectivity of delignification[12], the assays were performed in media containing 95% acetic acid. The media were kept at the normal boiling temperature without agitation at a liquor-to-wood ratio of 4 or 7 g liquor/g wood for the reaction time considered. Catalyst (HCl) concentration and reaction time were considered as operational variables and assayed at three levels, according to a full factorial design (see Table I). The dependent variables considered were pulp yield, Klason lignin content, cellulose

content, hemicellulose content, percentage of initial hemicelluloses converted to sugars and percentage of initial hemicelluloses converted to furaldehyde. Additional data concerning the contents of acetyl groups and soluble lignin in pulps and the conversion of cellulose into glucose or (hydroxymethyl)furaldehyde were also determined for further analytical characterization of pulps and liquors (data not shown).

TABLE I
Operational conditions and experimental results of Acetosolv treatment carried out at the normal boiling temperature in media containing 95% acetic acid

Exper. No.	Liquor -to- wood ratio g/g	Independent variables			Dependent variables				
		HCl[a] %	time min	pulp yield[b]	Klason lignin[c] %	Cellu- lose[d] %	Hemi- celluloses[e] %	HCHS[f] %	HCF[g] %
1	4	0.2	60	62.3	13.6	66.7	8.2	20.5	9.1
2	4	0.2	75	59.4	11.2	71.0	8.1	19.1	10.2
3	4	0.2	90	57.1	9.8	69.7	6.9	18.6	12.3
4	4	0.3	60	56.3	7.3	69.1	7.2	24.6	17.4
5	4	0.3	75	54.0	6.8	71.7	6.5	24.1	16.4
6	4	0.3	90	52.2	7.0	69.8	5.8	24.0	24.4
7	4	0.4	60	56.0	9.5	68.9	6.2	15.2	12.5
8	4	0.4	75	56.5	7.4	68.9	6.3	16.2	13.2
9	4	0.4	90	54.5	7.7	73.5	5.9	16.5	16.5
10	7	0.2	60	54.4	9.7	70.9	6.7	24.1	15.9
11	7	0.2	75	55.2	8.5	72.3	6.0	22.6	17.5
12	7	0.2	90	52.4	5.3	77.3	5.9	25.1	25.9
13	7	0.3	60	54.5	6.6	69.5	7.0	27.6	17.1
14	7	0.3	75	52.5	4.9	73.5	6.0	22.3	24.3
15	7	0.3	90	51.1	4.0	72.6	5.6	22.8	24.5
16	7	0.4	60	53.7	7.7	73.7	5.7	23.5	21.4
17	7	0.4	75	52.7	7.6	73.4	5.4	18.1	21.7
18	7	0.4	90	54.5	6.2	67.7	4.9	22.6	21.8

Definitions, nomenclature and units: [a] Concentration of catalyst expressed as g HCl/100 g liquor. [b] Pulp yield expressed as g pulp/100 g wood, o. d. basis. [c] Expressed as g Klason lignin/100 g pulp, o. d. basis. [d] Expressed as g cellulose/100 g pulp, o. d. basis. [e] Expressed as g hemicelluloses/100 g pulp, o. d. basis. [f] Per cent of hemicelluloses converted into hemicellulosic sugars. [g] Per cent of hemicelluloses converted into furfural.

From this point of view, pulp yield and pulp composition provided the most important information. Owing to the structure of experimental design, the interrelationships between dependent, VD, and independent, VI, variables can be expressed by equations involving linear, interaction and second-order terms according to the generalized equation:

$$
\mathrm{VD}_i = b_{0i} + \sum_{j=1}^{r} b_{ji} \left[\frac{2(\mathrm{VI}_j - \mathrm{VI}_{j\,\mathrm{med}})}{\mathrm{VI}_{j\,\mathrm{max}} - \mathrm{VI}_{j\,\mathrm{min}}} \right] +
$$

$$
+ \sum_{j=1}^{r} \sum_{k \geq j}^{r} b_{jki} \left[\frac{2(\mathrm{VI}_j - \mathrm{VI}_{j\,\mathrm{med}})}{\mathrm{VI}_{j\,\mathrm{max}} - \mathrm{VI}_{j\,\mathrm{min}}} \right] \left[\frac{2(\mathrm{VI}_k - \mathrm{VI}_{k\,\mathrm{med}})}{\mathrm{VI}_{k\,\mathrm{max}} - \mathrm{VI}_{k\,\mathrm{min}}} \right]. \tag{1}
$$

Coefficients in this equation were calculated from experimental data by multiple regression using the least squares method. This methodology allows the calculation of the dependent variables for given values of the operational variables[19–21] and it has been previously applied to the empirical modelling of organosolv pulping[12,19,22,23]. Figure 1 shows a comparison between experimental and calculated values of the most important dependent variables affecting the studied process, and confirms the ability of the models derived from Eq. (*1*) to give a quantitative interpretation of the experimental trends.

The pulp yields obtained in experiments 1 to 3 of Table I were higher than 57%, suggesting that improved results could be achieved under harsher operational conditions. Higher HCl concentrations and/or higher liquor/wood ratios led to lower pulp yields (in the range 51.1–56.3%) and defined the optimum operation zone.

The Klason lignin content of samples confirmed the above findings: in experiments 1 to 3, the lignin percentage in pulps (9.8–13.6%) was higher than in experiments 4–18. The lignin percentage of samples obtained in experiments 4 to 6 (6.8–7.3%) were lower than those reached using higher catalyst concentrations at the same liquor-to-wood ratio (experiments 7 to 9, which led to pulps with 9.5–7.7% Klason lignin). This fact is confirmed by the empirical model developed for the Klason lignin content in pulps for experiments carried out with 4 g liquor/g wood (Fig. 2a). The response surface showed a minimum in lignin content clearly defined for a reaction time about 84 min and 0.32% HCl. This behaviour can be justified on the basis of lignin repolymerization reactions, occurrence of which in

Acetosolv pulping has been previously reported[18]. Lignin repolymerization was less important in experiments carried out at higher liquor-to-wood ratios (assays 10 to 18 of Table I) owing to lower concentrations of lignin fragments in the pulping media (see model predictions in Fig. 2b). The sample with lowest lignin content (4.0%) was obtained in experiment 15, which was carried out with 0.3% HCl for 90 min at the highest liquor-to-wood ratio used in this set of experiments (7 g/g). This result is in the
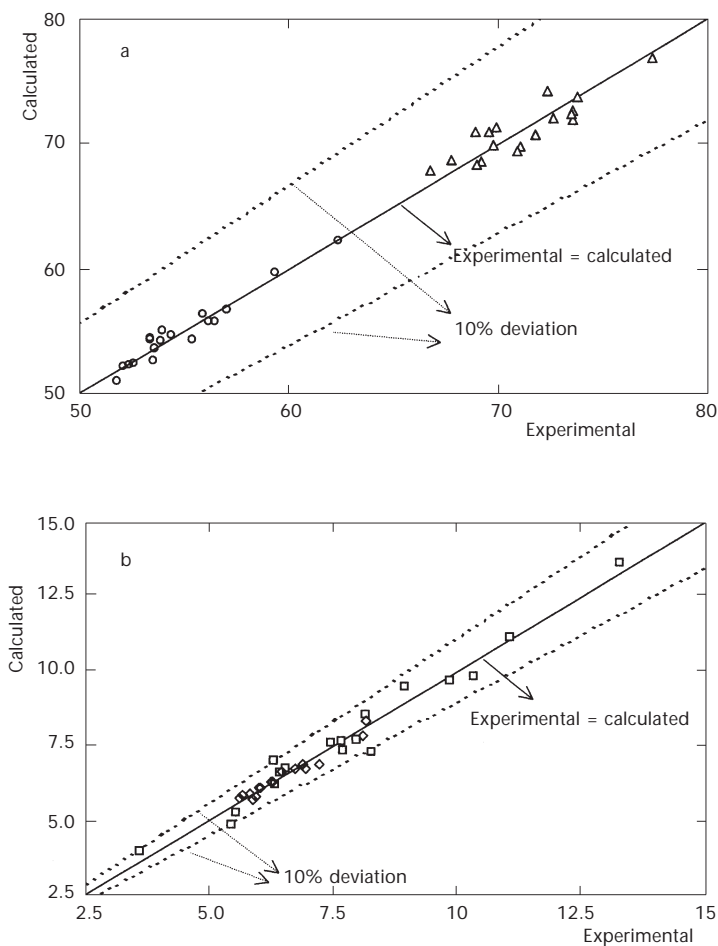

FIG. 1
Comparison between the experimental and calculated values of the most important experimental variables involved in this study. a Pulp yield (○), % cellulose (△); b % Klason lignin (□), % hemicelluloses (◇)

range of the best data reported for *Eucalyptus* wood pulping in acetic acid media[12,24].

As expected, the pulp with the lowest cellulose content was obtained in experiment 1, which was performed under the mildest operational conditions. The rest of samples treated with 4 g liquor/g wood (experiments 2 to 9) gave values in the range 68.9–73.5. Operating with 0.2 or 0.4% HCl, the cellulose content of samples was higher for experiments with longer reaction time, whereas small effects were caused by the reaction time in ex-
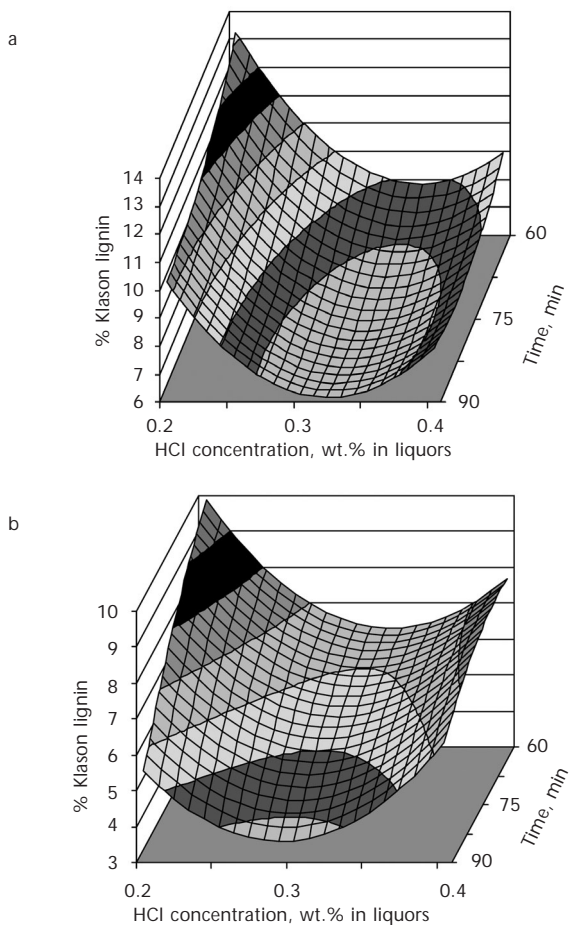

FIG. 2

Predicted dependence of the Klason lignin content of pulps on the most influential operational variables. a Results calculated for experiments carried out with 4 g liquor/g wood; b results calculated for experiments carried out with 7 g liquor/g wood

periments carried out with 0.3% HCl. The cellulose content of samples increased when the liquor-to-wood ratio was fixed at 7 g/g, but the results varied within a limited range (67.7–77.3%). The general trends of experimental data suggested that the best conditions for treatments corresponded to low catalyst concentrations and prolonged reaction times (for example, experiment 12) or to high catalyst concentrations and short reaction times (for example, experiment 16).

The hemicellulose content of pulps decreased with the severity of the operational conditions from 8.2% in assay 1 to 4.9% in assay 18. In experiments carried out with 4 g liquor/g wood, the hemicellulose removal was markedly affected by both reaction time and catalyst concentration, as it can be seen from the model predictions shown in Fig. 3. The duration of treatments was more influential when operating at low catalyst concentrations, whereas the main effects associated with the catalyst concentration were observed when the HCl percentage of liquors was increased from 0.2 to 0.3–0.35%.

The experimental data listed in Table I show that the contents of lignin, cellulose and hemicellulose averaged at 85.3 wt.% of pulps. In order to find an explanation for this finding, two additional fractions (acetyl groups and soluble lignin) were determined. The experimental results obtained for acetyl groups (4.4–7.5 wt.%) explained a significant part of the imbalance, and showed that a significant acetylation occurred during the Acetosolv treatments. On the other hand, soluble lignin accounted for 0.7–1.6 wt.%
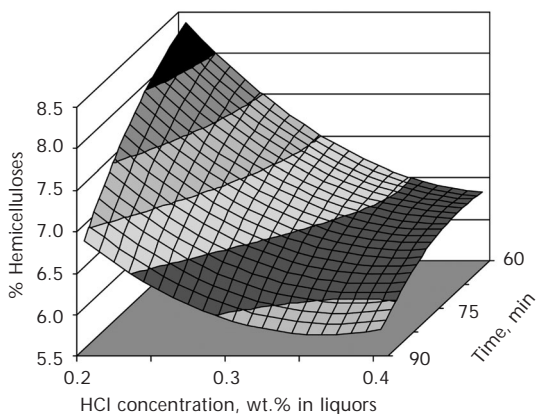

FIG. 3

Calculated dependence of the hemicellulose content of pulps on the most influential operational variables for the first Acetosolv stage. Liquor-to-wood weight ratio = 4 g/g

of samples, but no coherent variation with the experimental variables was observed.

Pulping liquors were assayed for marketable hemicellulose-degradation products (hemicellulosic sugars and furaldehyde). In order to provide comparative data, concentrations of both sugars and furaldehyde are expressed in terms of hemicellulose conversion (see Table I). Experiments 6 and 12 were most interesting from the point of view of byproduct generation. In both cases, hemicellulosic sugars and furaldehyde accounted together for 48.4–51.0% of the initial hemicelluloses after stoichiometric correction. As it was found in earlier studies[13,24], a significant part of hemicelluloses was degraded to unknown products in all the experiments.

Additional data were obtained on the glucose and (hydroxymethyl)-furaldehyde concentrations of pulping liquors (data not shown) in order to check the extent of cellulose degradation. The experimental results showed that less than 1% of the initial cellulose was converted into glucose or (hydroxymethyl)furaldehyde, confirming excellent selectivity of the Acetosolv delignification towards cellulose degradation.

Two-Stage Acetosolv Processing of Wood

Based on the experimental results listed in Table I, the conditions of experiment 8 (4 g liquor/g solid, 0.4% HCl, 75 min reaction time) were selected for obtaining the pulp to be used as a substrate in the subsequent pulping step owing to its favourable balance between pulp yield (56.5%) and lignin content (7.4%). Even if pulps with lower lignin content were obtained working at 7 g liquor/g solid (for example, in experiment 15), it was considered that this benefit was not sufficient to compensate the drawback derived from the higher amount of solvent needed.

Pulps obtained under selected conditions were subjected to harsher treatments either at the normal boiling temperature or at 130 °C. At first results obtained at the normal boiling temperature will be discussed. The media contained 0.4 or 1% HCl in 95% acetic acid solutions (liquor-to-solid ratio, 4 g/g) and delignification took 60–180 min (Table II). The effects of treatments were measured by the same experimental variables as before, but the results concerning the concentrations of hemicellulosic sugars and furaldehyde are omitted owing to the limited hemicellulose content of the starting pulp. Poor delignification was achieved when the second pulping stage was carried out at atmospheric pressure at 4 g liquor/g solid (experiments 19 to 26 in Table II). The lignin content in the limits of 5.2–6.2% with an average value of 5.7% reached in these experiments was higher

than the best one obtained in a single treatment with 7 g liquor/g solid (see experiment 15 in Table I). The reasonable pulp yield reaching an average value of 85.8% (based on the initial o. d. mass of pulp), the improved cellulose content and the remarkable hemicellulose removal obtained in a second Acetosolv step performed at atmospheric pressure were not sufficient to justify the interest in this operational procedure.

Since lignin repolymerization can play a significant role in the second pulping stage, a higher liquor-to-solid ratio (6 g/g) was also explored in treatments at the normal boiling temperature, which were carried out under the same conditions as before (see Table II). The lowest lignin contents (in the range 3.9–4.3%) were obtained in experiments 28, 30 and 33. These experiments led to pulps with improved cellulose contents (78.1–80.4%) and percentages of hemicelluloses in the range 3.7–4.3%.

TABLE II
Operational conditions[a] and experimental results of a second Acetosolv treatment carried out at the normal boiling temperature in media containing 95% acetic acid (see Table I for nomenclature)

Exper. No.	Liquor -to- solid ratio g/g	Independent variables			Dependent variables		
		HCl %	time min	pulp yield	Klason lignin %	Cellulose %	Hemicelluloses %
19	4	0.4	60	86.9	5.4	72.5	5.2
20	4	0.4	90	89.0	5.5	70.6	5.3
21	4	0.4	120	82.8	6.0	71.8	4.6
22	4	0.4	180	86.4	5.2	73.1	4.5
23	4	1	60	87.8	6.0	71.7	4.0
24	4	1	90	89.5	5.9	70.5	4.3
25	4	1	120	85.0	5.6	76.8	4.1
26	4	1	180	79.1	6.2	79.2	2.7
27	6	0.4	60	84.4	6.0	79.0	3.6
28	6	0.4	90	82.5	4.2	80.4	3.8
29	6	0.4	120	85.1	6.7	75.7	4.3
30	6	0.4	180	84.9	4.3	78.1	4.3
31	6	1	60	82.2	6.2	81.1	2.3
32	6	1	90	81.0	5.1	75.1	2.8
33	6	1	120	84.7	3.9	78.8	3.7
34	6	1	180	82.6	5.1	74.9	4.4

[a] Experiments carried out at 4 g liquor/g wood.

The effects obtained at 130 °C were assessed by means of an optimized experimental design with minimum void volume[25], in which 3 operational variables (liquor-to-solid ratio, % HCl and reaction time) were explored at 3 levels. The results are listed in Table III. In the same way as observed for treatment at atmospheric pressure, the liquor-to-solid ratio had an important effect on the degree of delignification. The experiments performed with 4 g liquor/g solid (experiments 35 to 38) led to pulps with 5.3–7.5% of Klason lignin and cellulose contents in the range 75.9–79.6%. When the liquor-to-solid ratio was increased to 6 or 8 g/g, delignification was significantly enhanced for selected combinations of catalyst concentration and reaction time. Pulps from experiments 41 and 46 (having Klason lignin contents of 3.0 and 2.3%) were the best obtained in treatments at 6 and 8 g liquor/g solid, respectively. Even if favourable cellulose contents were

TABLE III
Operational conditions and experimental results of a second Acetosolv treatment carried out at 130 °C in media containing 95% acetic acid (LSR = liquor-to-solid ratio, o. d. basis; see Table I for additional nomenclature)

Exper. No.	Independent variables			Dependent variables			
	LSR g/g	HCl %	time min	pulp yield[a]	Klason lignin, %	cellulose %	hemicelluloses %
35	4	0.2	30	88.3	5.3	78.2	4.1
36	4	0.4	15	86.2	6.8	75.9	4.1
37	4	0.4	45	81.3	7.5	78.4	1.7
38	4	0.6	30	84.4	6.4	79.6	2.6
39	6	0.2	15	87.1	6.3	78.5	3.7
40	6	0.2	45	82.6	3.9	79.5	2.4
41	6	0.4	30	81.9	3.0	79.2	2.2
42	6	0.6	15	83.8	6.2	71.9	2.5
43	6	0.6	45	78.4	7.3	72.7	1.0
44	6	0.6	30	80.2	4.8	74.8	1.7
45	8	0.2	30	83.8	6.1	75.7	2.6
46	8	0.4	15	84.6	2.3	81.5	2.8
47	8	0.4	45	78.8	5.9	75.3	1.9
48	8	0.6	30	77.1	6.3	79.9	2.1

[a] Based on the mass of o. d. pulp entering the second stage.

achieved in both cases (79.2 and 81.5%), the most important feature was the low hemicellulose content of pulps (2.2 and 2.8%).

As it was previously observed for single Acetosolv treatments, the joint contribution of lignin, cellulose and hemicelluloses obtained after two-step processing accounted only for a fraction of the overall pulp yield. Most of the imbalance can be again justified on the basis of the presence of acetyl groups, which accounted for 7.4–14.0 wt.% of pulps obtained in experiments 19 to 48.

SYMBOLS

b	regression coefficient
LSR	liquor-to-solid ratio, g/g
VD	dependent variable
VI	independent variable

Subscripts

i, j, k	employed for specification of variables and coefficients
max	upper limit of the variable's variation range
min	lower limit of the variable's variation range
med	middle of the variable's variation range
r	number of independent variables affecting the considered dependent variable

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