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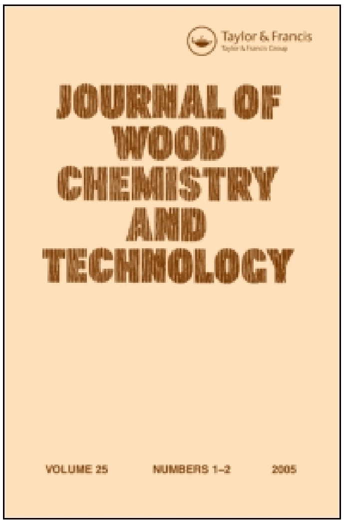

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# CELLULOSE FROM SOFTWOOD VIA PREHYDROLYSIS AND SODA/ANTHRAQUINONE PULPING

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## ABSTRACT

A two stage process based on a hydrolytic pretreatment and a soda/anthraquinone pulping stage has been studied to produce bleachable-grade cellulose from residual softwood sawdust, concretely a mixture of ground spruce *(Abies alba)* and pine *(Pinus insignis)*. The hydrolytic pretreatment, which is carried out in an isothermal plug-flow reactor, solubilizes the hemicelluloses and substances of low molecular weight, and partially depolymerizes the lignin which can then be more easily extracted during the pulping stage. Soda/AQ pulping was performed on the pretreated fiber in a stirred batch reactor. The resulting cellulose pulps have low contents of residual hemicelluloses and ash, and a low enough amount of residual lignin which means that a chlorine-free bleaching procedure may be used. The effect of the process variables on the chemical characteristics and yields of the unbleached cellulose are presented. The combination of an autohydrolytic pretreatment at 231 °C for 5.5 min and a pulping stage at 170 °C for 150 min using 0.1% of anthraquinone, results in a cellulose yield of 64% of the potential. Because of the pretreatment the cellulose is partially depolymerized. This cellulose has a kappa number of 16.6, a non detectable content of hemicelluloses by HPLC analysis, an ash content of 0.60%(w/w) and an average degree of polymerization of 300.

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## INTRODUCTION

Cellulose, which has a great number of potential uses, is the main component of lignocellulosic materials . Consequently, the upgrading of residual lignocellulosic materials is directly associated with the production of cellulose and cellulose derivatives. One field of application is the production of high purity cellulose appropriate for use in food products, pharmacy, veterinary, cosmetics and chemical derivatives.[1-5]

Processes for the production of pure cellulose are modifications of typical pulping and bleaching processes for the production of paper and related products. Normally they include pretreatment or controlled hydrolysis of the pulp in order to remove hemicelluloses, which in this case are not desired.

At present, new technology and environmental concerns are significantly changing pulping and bleaching processes.[6,7] One environmental concern is the use of sulfur compounds that produce air pollutants like hydrogen sulfide, mercaptans and organic sulfides. Another environmental concern is the chlorinated organic materials present in bleach-plant effluents.[8] Developed countries have imposed strict limits on the emission of these pollutants. All these factors are forcing the cellulose industry to develop alternative processes of pulping and bleaching that reduce, and even suppress, the presence of sulfur and chlorine compounds. One tried and tested method is anthraquinone pulping. [9] There are two main effects from which all possible applications of anthraquinone derive: the acceleration of alkaline pulping, and the stabilization of carbohydrates which results in higher yields of pulp.[10,11] Anthraquinone pulping addresses the abovementioned environmental concerns by totally eliminating sulfur compounds during the pulping stage, and reduces bleach plant emissions because of the extended delignification during the pulping stage. The reduction of the kappa number for softwoods to values lower than 30-35 allows the use of chlorine compounds to be decreased during bleaching.[12]

To produce high purity cellulose for the manufacture of cellulose-derived chemicals it is also necessary to separate the residual hemicelluloses remaining in the cellulose pulp. Therefore, classical pulping processes, which are designed to preserve the highest amount of hemicellulose in order to increase yield, must be modified for this purpose. Steam-aqueous treatments, which are mainly hydrolytic in nature, dissolve the hemicellulose fraction and other low molecular weight substances prior to the pulping stage, thus allowing the production of cellulose pulps with few residual hemicelluloses. This pretreatment also depolymerizes lignin, thus promoting extended delignification. The main aim of this work is to test the combination of a hydrolytic pretreatment and a soda-anthraquinone pulping in order to produce cellulose with a very low content of hemicellulose, and a kappa number lower than 30 to allow a chlorine-free bleaching sequence.

## METHODS

### Softwood Sawdust

The experiments were carried out using a homogeneous batch of ground softwood residues, spruce *(Abies alba)* and pine *(Pinus insignis)*, harvested in Lleida, Catalonia, in the north-east of Spain. The ground material was sieved to 100 mesh (150 µm) and had a moisture content of 7 % of the total weight. The average composition of seven different samples of the batch is listed in **Table 1** (in percent of w/w of dry lignocellulosics).

### Production of the Unbleached Cellulose

The sequence used in this work for the fractionation of the softwood sawdust is shown in **Figure 1**. The process is divided into two blocks: the hydrolytic pretreatment and the soda/anthraquinone pulping stage. The aim of the process was to produce bleachable-grade cellulose with a minimum content of residual hemicellulose. The hemicellulose and the lignin fractions can be partially recovered during the process.

### Hydrolytic Pretreatment

The hydrolytic pretreatment was conducted in a continuous tubular reactor capable of processing up to 100 kg $h^{-1}$ of aqueous suspensions of ground lignocellulosics with a solid content up to 25%, depending on the lignocellulosic

**TABLE 1**
Average Composition and 95% Confidence Interval for the Softwood Mixture. Results Based on 100 g of Dry Softwood Mixture (% DSB)

| Fraction | Average value | Confidence limit |
|---|---|---|
| Ash | 0.4 | 0.1 |
| Hot water extractives | 7.4 | 1.4 |
| Ethanol/Toluene extractives | 3.3 | 1.4 |
| Klason lignin | 25.1 | 0.8 |
| Glucose | 38.2 | 0.7 |
| Xylose | 5.9 | 0.3 |
| Galactose | 4.1 | 0.2 |
| Arabinose | 6.6 | 0.3 |
| Mannose | 12.0 | 0.8 |

characteristics. A complete description of the equipment has been previously published.[13] A total of 14 experiments were conducted at temperatures ranging from 176 to 231 °C, with residence times for the hot slurry between 2.5 and 5.5 min. A solid concentration of 7% (w/w) was used in all the experiments. The pretreated slurry was filtered, and the fiber washed at 90 °C for 15 min in order to remove the water-soluble products.

## Soda-Anthraquinone Pulping

Soda and soda/anthraquinone pulps were prepared in a 300 mL stirred batch reactor. Initially, eight different experiments using the untreated lignocellulosic were carried out to set the best conditions for the delignification process. Two additional experiments were carried out with pretreated lignocellulosic material (T=223 °C, t=4.3 min) in order to observe the pretreatment impact on the soda versus soda/AQ comparison. The experimental plan covered temperatures of 160 and 170 °C, a residence time at these temperatures from 60 to 150 min, heating times from 15 to 75 min, alkali loads of 20 and 40% DSB (Dry Solid Basis), anthraquinone loads of 0.1% DSB, and a liquor to wood ratio of 20:1 and 10:1. All experiments were performed at a stirrer speed of 430 rpm. The pulps were filtered and washed with hot water. Lignin was recovered from the black liquor by acid precipitation.

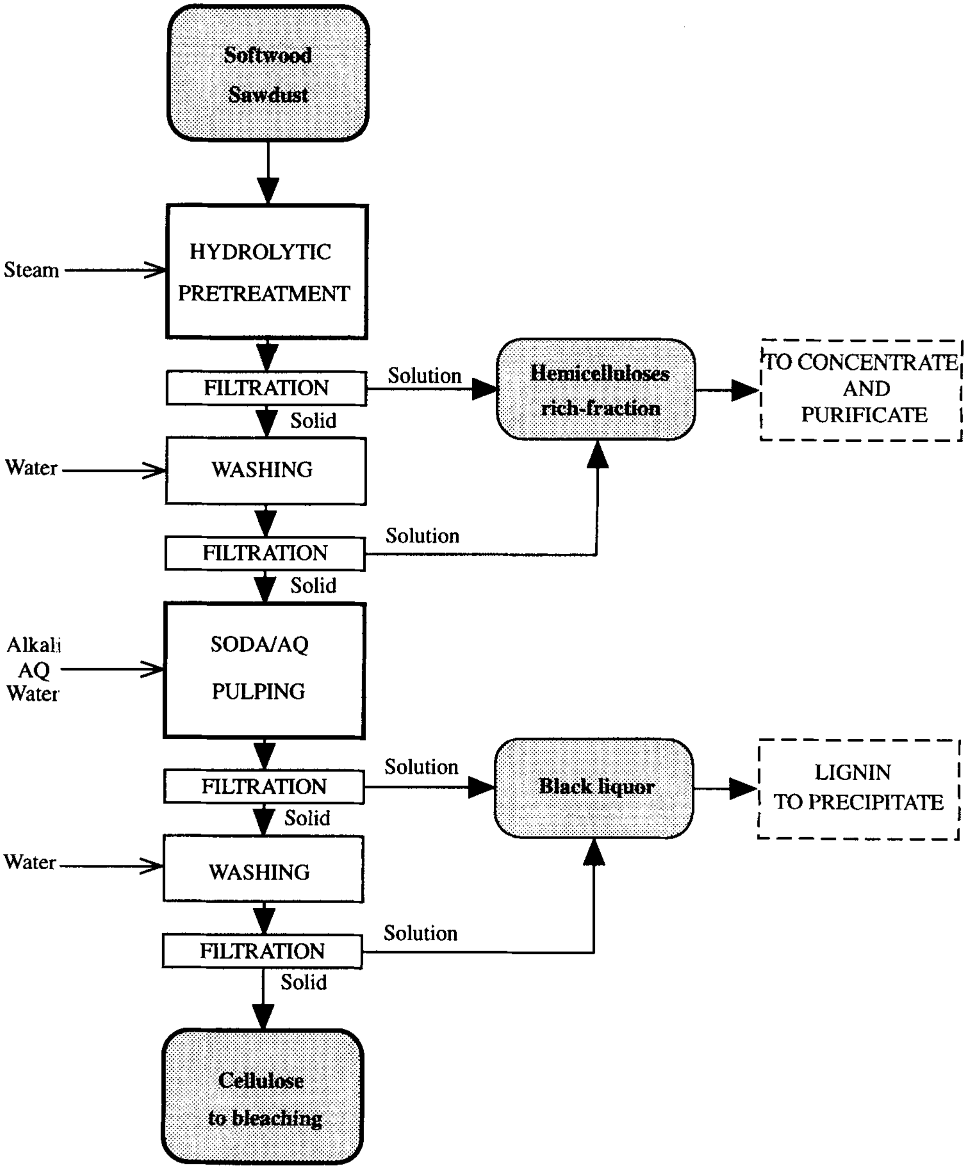

**FIGURE 1.** Block diagram of unbleached cellulose production.

The softwood prehydrolized at different severities was pulped in the following conditions which are the best ones found as will be shown below: 170 °C, a residence time of 150 min, a heating time of 25 min, a liquor-to-wood ratio of 10:1 and alkali and anthraquinone loads of 40% NaOH and 0.1% AQ, both in dry solid basis.

## Analytical Procedures

The original softwood mixture, the pretreated substrate and the Soda/AQ pulps were chemically analyzed using the following standard methods: ASTM D-1348 for moisture content; TAPPI T 15 os-80 for ash content; TAPPI T 207 om-81 for hot-water extractives and TAPPI T 204 os-76 for ethanol/toluene extractives. Klason lignin was measured in the extractive-free samples with the TAPPI T 222 om-83 standard method. The carbohydrate analysis of the softwood residues, pretreated and pulped samples was performed by HPLC.[13] The cellulose content was calculated as anhydrous glucose with a correction due to the high glucomannan fraction. Typically the ratio between mannose and glucose in softwood glucomannans is 3:1;[1] consequently the value corresponding to a third of the weight of mannose is subtracted from the overall value of anhydrous glucose and added to the hemicellulose fraction. In order to carry out the mass balance for softwood residues, the total amount of soluble products was calculated by evaporation to dryness at 60 °C of various aliquots of the liquid.

The content of residual lignin in the pulp was measured using the kappa number method (TAPPI T226 os-76).

Holocellulose was prepared from an extractive-free sample by chlorite delignification [14], and α-cellulose was isolated from holocellulose by extraction with concentrated sodium hydroxide according to the TAPPI T-203 os-74 method.

The viscosity-average degree of polymerization, DPv, of the cellulose remaining in the pulp were investigated in the α-cellulose fraction. The degree of polymerization was calculated from the intrinsic viscosity according to the relationship in equation (1).[15] The intrinsic viscosity, $[\eta]_{CED}$, was measured in a 0.5 M solution of cupriethylenediamine hydroxide (CED) using the ISO 5351/1-1981 standard.

$$DP_V = 1.90 \cdot [\eta]_{CED} \tag{1}$$

**TABLE 2**
Typical Experimental Conditions for Soda-Anthraquinone Pulping. All Percentages Refer to Dry Wood (w/w).

| Species(reference) | alkali (%) | liquor wood | % alkali in liquor | Temp. (°C) | Time (min) heating | Time (min) pulping | AQ (%) | Kappa number | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| Softwood (9) | 20(TA) | 4:1 | 5.0 | 180 | 60 | 50 | 1.0 | 27.5 | 51.1 |
| *Picea mariana* (17) | 20(EA) | 4:1 | 5.0 | 170 | 90 | - | 0.25 | 30.0 | 50.0 |
| *Picea abies* (18) | 20(TA) | 5:1 | 4.0 | 173 | 30 | 60 | 1.0 | 45.5 | 52.0 |
| *Pinus silvestris* (19) | 20(TA) | 4:1 | 5.0 | 170 | 150 | 90 | 0.5 | 50.6 | 35.6 |
| *Picea abies* (19) | 20(TA) | 4:1 | 5.0 | 170 | 150 | 90 | 0.5 | 52.0 | 39.2 |
| *Pinus pinaster* (16) | 21(TA) | 4:1 | 5.3 | 170 | 90 | 90 | 0.3 | 32.0 | 45.7 |
| Softwood (14) | 18(EA) | 4:1 | 4.5 | 170 | 60 | 90 | 0.1 | 58.9 | - |

## RESULTS AND DISCUSSION

### Pulping of the Untreated Softwood Mixture

The soda-anthraquinone process depends on several operation variables, such as temperature, alkali load, anthraquinone addition, heating rate, cooking time and liquor to wood ratio, which directly affect the yield and the properties of the pulp. The process also depends on the digester characteristics and the lignocellulosic substrate. Consequently, it was necessary to establish which operation conditions were able to yield bleachable-grade pulps. In order to use a reduced number of experiments, a sequential searching strategy was developed, aimed at reducing the kappa number and simultaneously maximizing pulp yield. **Table 2** shows some of the most common values cited in the bibliography [9,12,16-19] for the operating conditions of soda/anthraquinone pulping of softwood samples. Alkali loads remain almost constant at around 20% DSB while anthraquinone addition varies from 0.1% DSB to 1.0% DSB. However, in recent works, the tendency is to use a charge of up to 0.1% DSB since higher amounts of anthraquinone do not lead to a substantial decrease in the kappa no. but do lower the bleachable properties of the pulp. Moreover, AQ loads above 0.1% DSB exceed the maximum level which the US Food and Drug Administration mandates for the production of food-grade paper products.[16] The maximum operating temperature reaches 180 °C, although the

**TABLE 3**

Experimental Conditions Used for the Soda and Soda-Anthraquinone Pulping of the Original Softwood Mixture and the Pretreated Sample (T=223 °C, t=4.3 min). Results are Based on 100 g of Dry Softwood Mixture (% DSB).

| Experiment | 1 | 2 | 2b | 3 | 4 | 4b | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|---|
| alkali (%DSB) | 20 | 20 | 20 | 40 | 20 | 20 | 40 | 40 | 40 | 40 |
| liquor:wood ratio | 20:1 | 20:1 | 20:1 | 20:1 | 20:1 | 20:1 | 20:1 | 20:1 | 20:1 | 10:1 |
| alkali in liquor (%) | 1 | 1 | 1 | 2 | 1 | 1 | 2 | 2 | 2 | 4 |
| temperature (°C) | 160 | 170 | 170 | 170 | 170 | 170 | 170 | 170 | 170 | 170 |
| time to temperature (min) | 15 | 25 | 25 | 25 | 25 | 25 | 25 | 75 | 25 | 25 |
| time at temperature (min) | 60 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 150 | 150 |
| H-factor (h) | 725 | 2700 | 2700 | 2700 | 2700 | 2700 | 2700 | 2920 | 4400 | 4400 |
| AQ load (%) | - | - | - | - | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| kappa number | 156 | 137 | 162 | 92.7 | 105 | 111 | 57.4 | 54.4 | 46.3 | 28.5 |
| pulp yield (%) | 73.1 | 72.8 | 46.2 | 52.5 | 68.3 | 43.5 | 47.1 | 46.5 | 44.7 | 40.7 |

typical values are situated around 170 °C, with heating times varying from 30 to 150 min and residence time at this temperature from about 60 to 120 min. The liquor to wood ratio changes between 5:1 and 4:1, but due to the geometry of the reactor used in this study and the sample characteristics it was not possible, due to mixing problems, to reach a liquor to wood ratio lower than 10:1. For this reason, higher alkali loads than normal were used to maintain the alkali concentration in the liquor.

A first set of experiments used the conventional soda pulping process, while a second set included anthraquinone in order to evaluate its effectiveness in kappa reduction.[19,20] **Table 3** shows the pulping conditions used for the untreated and pretreated softwood sawdust, and also the kappa no. and the pulp yield (% o.d. wood). The H-factor[21] modified for soda processes with zero sulfidity,[22] as shown in equation (2), was also calculated in order to group the effect of the pulping temperature, the heating rate and the pulping time in a single operation variable.

$$H(h) = 3.15 \cdot 10^{20} \cdot \int_0^{t[h]} \exp\left(\frac{-17614}{T[K]}\right) \cdot dt \qquad (2)$$

## Maximum Temperature and Residence Time. Overall Effect.

Experiments 1 and 2, **Table 3**, show the overall influence of the reaction temperature and residence time on the yield and kappa number of the pulp. The kappa no. decreases from 156 at a temperature of 160 °C for 60 min (H-factor=725. Including heating period) to 137 at 170 °C for 90 min (H-factor=2700). Consequently, the kappa number is observed to decrease when the H-factor is increased, although the kappa numbers obtained are not sufficiently low. At the same time, the pulp yield remains approximately constant in these operating conditions. The heating rate does not seem to significantly modify the kappa no. in comparison to other variables as can be observed in experiments 5 and 6. The kappa no. decreases from 57 (H-factor=2700) to 54 (H-factor=2920). The pulp yield remains practically constant at around 47%. Cooking time directly affects the delignification rate. Experiments 5 and 7 show how the kappa no. varies from 57 at 90 min to 46 at 150 min. The H-factors were 2700 and 4400 respectively. There is a small reduction in the pulp yield in these operation conditions, which implies that higher severities in the delignification process do not cause further solubilization.

## Alkali Load

Experiments 2 to 5 were performed at constant H-factor and show the effect of the alkali when it doubles from 20 to 40% DSB. The kappa no. decreases from 137 to 93 for the soda pulps, and from 105 to 57 for the soda/AQ pulps. This represents an average decrease in the kappa number of 46 points. Moreover, pulp yield decreases from 73 to 53% and from 68 to 47%, respectively (a mean decrease of 20%). These values indicate that a considerable amount of the lignin originally present in the untreated softwood is solubilized when the alkali load is increased to 40%, which in this case represents a concentration of 2% of alkali in liquor. Presumably, even more of the hemicellulose fraction is also solubilized.

## Anthraquinone Addition

Experiments 2 to 5 also show the effect of anthraquinone, 0.1% DSB, at different alkali loads. The kappa no. decreases from 137 in experiment 2 to 105 in experiment 4 at an alkali load of 20% DSB, while at 40% the kappa no. decreases from 93 in experiment 3 to 57 in experiment 5. The mean decrease in kappa number is of 34 points. Pulp yield decreases from 73 to 68% and 53 to 47%, respectively (a mean decrease of 5.5%). As can be observed, the combination of high alkali load and anthraquinone improves delignification although there is a considerable reduction in pulp yield, mainly due to the effect of the alkali charge.

Experiments 2b and 4b were also performed at constant H-factor in the same conditions as experiments 2 and 4 but with pretreated samples (T=223 °C, t=4.3 min). The kappa number decreases from 162 in experiment 2b to 111 in experiment 4b. This represents a decrease of 51 points and shows that the effect of adding AQ is also considerable in the case of pretreated samples.

### Liquor to Wood Ratio

Experiments 7 and 8 show the effect of the liquor to wood ratio when it changes from 20:1 to 10:1. The kappa no. decreases from 46 to 29 while the pulp yield goes down from 45 to 41%, mainly as a consequence of the loss of lignin. Since the alkali charge does not vary, an increase in the concentration of lignocellulosics leads to a rise in alkali concentration in the liquor-wood interphase, in this case from 2 to 4% NaOH, and consequently an improvement in the delignification. Results obtained in experiment 8 show a low kappa number compared to experiments with softwood samples reported in literature. Pulp yield is in the usual range.

## Effect of the Hydrolytic Pretreatment

The operation conditions used for pretreating the softwood sawdust in the tubular reactor under autohydrolysis conditions are shown in **Table 4**, which also shows the amount of solubilized lignocellulosic in water and the composition of the insoluble fraction. The severity of the hydrolytic pretreatment was measured through the $R_0$ parameter, equation (3) [23], which groups the treatment temperature and time into a single variable.

$$R_0[\min] = \int_0^{t[\min]} \exp\left(\frac{T[^\circ C]-100}{14.75}\right)\cdot dt \qquad (3)$$

**Figure 2** shows the amount of solubilized lignocellulosic and the composition of the obtained fiber in dry solid basis (%DSB) as a function of the pretreatment

TABLE 4
Pretreatment of the Softwood Mixture by Autohydrolysis in the Continuous Tubular Reactor. Operating Conditions, Yield and Chemical Composition of the Pretreated Fiber. Results are Based on 100 g of Dry Softwood Mixture (% DSB). Other Anhydrous Sugars Represent Xylose, Galactose, Arabinose and Mannose.

| Experiment | 1-S | 2-S | 3-S | 4-S | 5-S | 6-S | 7-S | 8-S | 9-S | 10-S | 11-S | 12-S | 13-S | 14-S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pretreatment | | | | | | | | | | | | | | |
| Temperature (°C) | 227 | 227 | 223 | 187 | 221 | 215 | 231 | 176 | 191 | 198 | 225 | 217 | 229 | 231 |
| Time (min) | 2.0 | 4.8 | 4.3 | 3.1 | 5.4 | 3.0 | 5.5 | 2.5 | 3.1 | 2.9 | 2.9 | 2.8 | 4.8 | 3.0 |
| Severity (min) | 4.04 | 4.42 | 4.26 | 3.05 | 4.30 | 3.86 | 4.60 | 2.64 | 3.17 | 3.35 | 4.14 | 3.89 | 4.48 | 4.33 |
| Solubilization | 30.5 | 34.8 | 32.1 | 23.8 | 32.3 | 29.3 | 39.2 | 17.5 | 26.0 | 28.6 | 31.4 | 31.4 | 35.5 | 33.1 |
| Fiber composition | | | | | | | | | | | | | | |
| Anhydrous glucose | 34.7 | 38.8 | 37.4 | 34.8 | 38.0 | 36.6 | 33.1 | 35.6 | 34.6 | 36.0 | 37.2 | 37.7 | 34.5 | 33.5 |
| Other sugars | 9.5 | 5.0 | 8.3 | 13.3 | 7.9 | 10.6 | 4.4 | 17.7 | 12.9 | 10.9 | 8.7 | 9.0 | 5.6 | 8.4 |
| Ethanol/toluene ext. | 2.4 | 4.0 | 3.7 | 2.5 | 3.2 | 3.0 | 4.2 | 3.3 | 2.1 | 2.5 | 5.7 | 5.0 | 4.7 | 3.5 |
| Klason lignin | 21.7 | 19.9 | 20.5 | 23.8 | 21.8 | 21.4 | 18.2 | 24.0 | 23.7 | 22.9 | 20.7 | 21.1 | 19.2 | 20.0 |
| Total lignin | 24.1 | 23.9 | 24.2 | 26.3 | 25.0 | 24.4 | 22.4 | 27.3 | 25.8 | 25.4 | 26.4 | 26.1 | 23.9 | 23.5 |
| Cellulose | 33.1 | 37.6 | 36.1 | 32.5 | 36.7 | 34.6 | 32.0 | 32.3 | 32.5 | 34.3 | 35.5 | 36.1 | 33.1 | 32.1 |
| Hemicellulose | 11.1 | 6.2 | 9.6 | 15.6 | 9.2 | 12.6 | 5.5 | 21.0 | 15.0 | 12.6 | 10.4 | 10.6 | 7.0 | 9.8 |

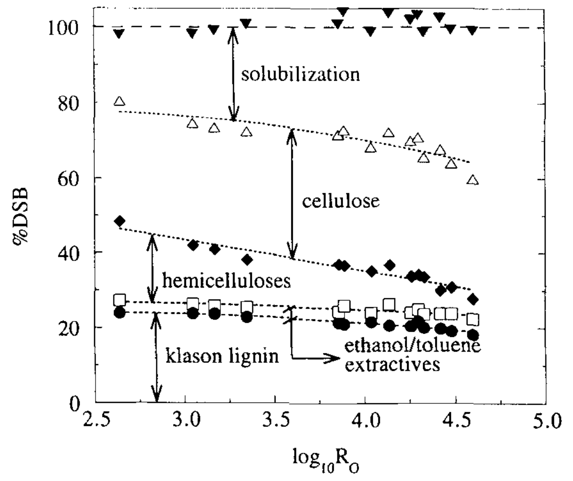

FIGURE 2. Effect of the pretreatment severity, expressed as $\log_{10}R_0$, on the solubilization of the softwood mixture and the composition of the solid fraction (The dashed lines only indicate trends). Results Based on 100 g of Dry Softwood Mixture (% DSB).

severity expressed as $\log_{10}R_0$ for the set of experiments reported in **Table 4**. Experiments show the influence of the reaction severity on the yield and chemical composition of the fiber. The solubilization of softwood sawdust after hydrolytic pretreatment and hot water washing increases continuously with pretreatment severity from a value around 18% DSB at $\log_{10}R_0 = 2.64$ (176 °C and 2.5 min) to 39% DSB at $\log_{10}R_0 = 4.60$ (231 °C and 5.5 min). Simultaneously, the content of cellulose, measured as anhydrous glucose corrected for the glucomannan content, does not change significantly when the pretreatment severity increases. It remains approximately constant over the temperature range covered. The pretreatment only depolymerizes cellulose but the extent of the depolymerization process is not high enough to solubilize a significant amount of the cellulose fraction in this severity range.

The amount of hemicellulose in the fiber decreases from 21.0% DSB at $\log_{10}R_0 = 2.64$, which represents around 64% of the original hemicellulose content, to a residual content of 5.5% at $\log_{10}R_0 = 4.60$, approximately only 17% of the initial content. In most cases at higher values of $\log_{10}R_0 = 3.0$ hemicellulose removal is higher than 50% of the initial content. The solubilization of hemicellulose during this stage is the key to the production of purified cellulose. At a severity above $\log_{10}R_0 = 4.4$ hemicellulose removal is more than 80% of the initial content.

The lignin content, considered in the case of the pretreated samples as the sum of the Klason lignin and the ethanol/toluene soluble fraction, decreases from 27.3% DSB at the lowest severity studied to 22.4% DSB at the highest. In pretreatments at low severity, up to $\log_{10}R_0 = 3.5$, some of the ethanol/toluene extractives may still be present in the substrate. This would explain why values for the lignin content are higher than the lignin content in the original sample. In the case of the sample pretreated at $\log_{10}R_0 = 4.60$ the loss in lignin is around 11% of the original content, or 27% if the Klason lignin is considered without the sum of the organic-soluble fraction. Although most of the lignin still remains in fiber, the effect of the increase in the pretreatment severity on the lignin fraction is considerable. The increase in temperature and reaction time partially depolymerizes the lignin content which therefore decreases because it is partially solubilized. This depolymerization improves later delignification.

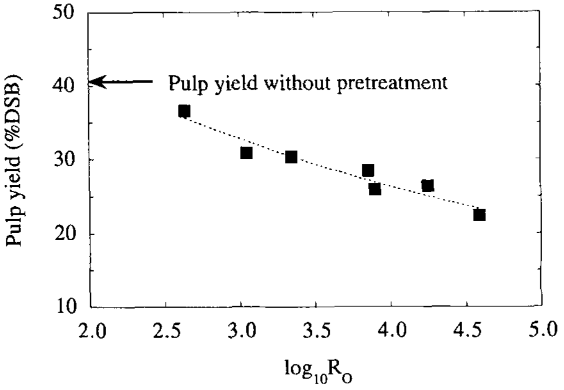

**FIGURE 3.** Effect of the pretreatment severity, expressed as $\log_{10}R_0$, on the global yield of unbleached cellulose pulp. (The dashed line only indicates trend). Results Based on 100 g of Dry Softwood Mixture (% DSB).

Soda/AQ Pulping of the Pretreated Samples

The overall yield of unbleached pulp after hydrolytic pretreatment and soda/anthraquinone pulping, with reference to the initial lignocellulosic sample in dry solid basis (% DSB), is shown in **Figure 3** as a function of the pretreatment severity ($\log_{10}R_0$). The yield of pulp decreases significantly when the pretreatment severity is increased. The yield of unbleached pulp decreases from a value of 36.6% DSB at $\log_{10}R_0 = 2.6$, which represents a decrease of around 10% in comparison to a non pretreated sample, to a value of 22.4% at $\log_{10}R_0 = 4.6$, which represents a decrease of around 44%.

**Figure 4** shows the evolution of the kappa number of the pulps produced from the pretreated samples as a function of the pretreatment severity. A considerable decrease in the kappa number is observed when the pretreatment severity increases. The kappa number decreases from a value of 19.8 at $\log_{10}R_0 = 2.64$ to a value of 16.0 at $\log_{10}R_0 = 4.26$ (T=223 °C and 4.3 min). At the highest pretreatment severity tested ($\log_{10}R_0 = 4.60$) the kappa number is 16.6. These values represent kappa reductions of 30, 44 and 42 % respectively,

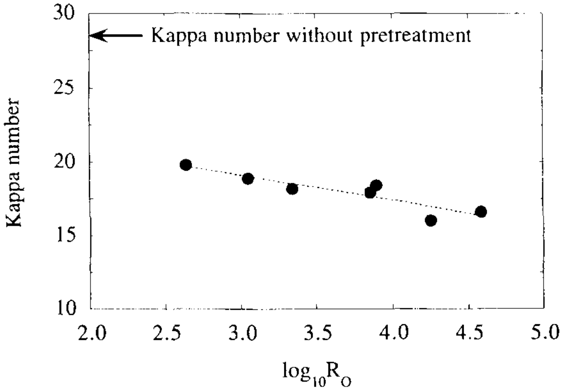

**FIGURE 4.** Effect of the pretreatment severity, expressed as $\log_{10}R_0$, on the kappa number of the unbleached cellulose pulp. (The dashed line only indicates trend).

compared to the value obtained for the pulp prepared from the original softwood mixture. Results show that hydrolytic pretreatment leads to a considerable decrease in the kappa number of the pulp and consequently an improvement in the pulping stage.

The loss in yield is due to, on the one hand, hemicellulose and lignin removal during the pretreatment, which is desirable, and to a slight decrease in the pulping stage yield when the pretreatment severity increases. A pretreatment with a severity higher than the maximum tested would represent an excessive loss in potential cellulose for very little further reduction in the kappa number.

**Table 5** shows the viscosity average degree of polymerization, DPv, of the α-cellulose remaining in the unpretreated sample, initially and after pulping, and when there is hydrolytic pretreatment at the highest severity ($\log_{10}R_0 = 4.60$), after pretreatment and pulping. The highest severity conditions of pretreatment were chosen to guarantee the effective removal of hemicelluloses, according to the main objective of this work. In this case, after a pretreatment of $\log_{10}R_0 = 4.60$, the residual hemicellulose content before pulping is only 5.5% DSB. This theoretically ensures the almost total loss of the hemicelluloses present in the original sample after the two stages.

TABLE 5

Viscosity average degree of polymerization, DPv, of the α-cellulose of pulps obtained after single or two stage pulping. (DPv of original softwood mixture = 700)

| Sample | DPv after pretreatment | DPv after pulping |
|---|---|---|
| Untreated | - | 450 |
| Pretreated (log R=4.60) | 330 | 300 |

In the case of the untreated sample the DPv of α-cellulose decreases from 700 to 450. The cellulose is partially degraded problably due to the alkali concentration and the H-factor[16,22].

On the other hand, the DPv number of the pretreated sample is seen to decrease mainly in the pretreatment stage. In this stage DPv decreases from a initial value of 700 to 330. Afterwards, in pulping stage, DPv only decreases from 330 to 300.

A complete characterization of the pulps from the softwood mixture and the sample pretreated at the highest severity tested was carried out in order to compare the effect of the pretreatment in the chemical composition of the cellulose pulp. **Figure 5** shows the chemical composition of the unprocessed softwood mixture free of extractives, the sample pretreated at $\log_{10}R_0 = 4.60$ and the pulps obtained from both samples, in comparison to 100 g of the initial softwood mixture (% DSB). A significant decrease in hemicellulose is observed in the unbleached cellulose pulp when the sequence pretreatment-pulping is carried out. In fact, the hemicellulose content in the pulp previously submitted to pretreatment was so low that it could not be detected by HPLC. The hemicellulose content in dry pulp obtained from the original softwood mixture was 22.6% (9.2% DSB).

The cellulose recovered after pulping, expressed as corrected anhydrous glucose, decreases from 90% (30.7% DSB) for the original softwood mixture to 64% (21.9% DSB) for the pretreated pulp. The decrease in lignin content is shown by the kappa number, specifically a value of 28.5 in the non pretreated sample and 16.6 in the pretreated one, which correspond to residual lignin contents of 1.8 and 0.6% DSB respectively. The ash content also decreases in the pretreated sample to a value of 0.14% DSB (0.25% DSB in the non pretreated sample) but the relative content in the unbleached pulp is approximately the same in both cases, around

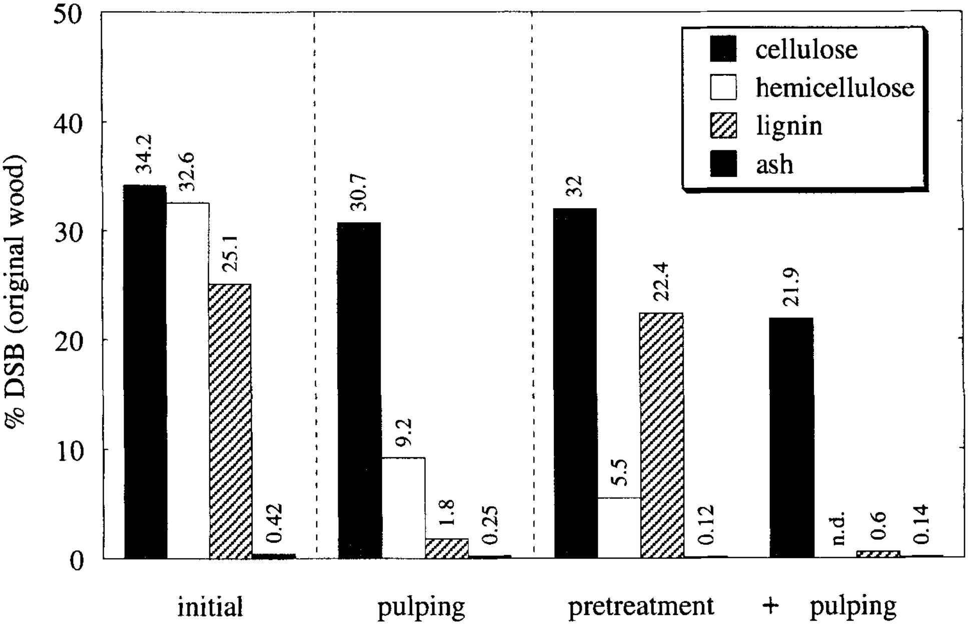

**FIGURE 5.** Comparison between the unbleached cellulose pulps obtained with a high severity pretreatment ($\log_{10}R_0$=4.60) or with no previous pretreatment. Evolution of the chemical composition of fiber obtained in each stage. Results Based on 100 g of Dry Softwood Mixture (% DSB).

0.60%. The residual lignin and the ash content can be reduced in later bleaching. Cellulose pulp purity is higher in the case of previous pretreatment although the yield decreases.

For the two stage process (pretreatment-pulping), the hemicellulose is mainly removed in the pretreatment stage. In comparison to dry initial solid basis, the hemicellulose content decreases from 32.6% to 5.5%. This represents a reduction of 83% in the original hemicellulose. The residual 17% of the hemicellulose is almost totally removed during the pulping stage. Lignin removal is mainly produced during the second stage, since only 12% of the original lignin is removed during the pretreatment stage. The lignin content decreases from 25.1 to 22.2% DSB, the organic-soluble fraction of the pretreated softwood being considered as a component of this fraction. After pulping, another 86% of the original lignin is extracted giving a residual value of 0.6% DSB. The main loss in cellulose is produced in the pulping stage as a result of the partial depolymerization of the cellulose fibers during the hydrolytic pretreatment, which then become partially soluble in the pulping liquor. The loss of cellulose in the pretreatment stage is only 6%, from 34.2 to 32.0% DSB, and 30% during pulping stage, from 32.0 to 21.9% DSB. The ash content decreases during the pretreatment from 0.43 to 0.13% DSB and remains practically constant during pulping.

## CONCLUSIONS

The process based on the combination of hydrolytic pretreatment and soda/anthraquinone pulping studied in this work is shown to be effective for obtaining cellulose pulps with a low kappa number and a very low content of residual hemicelluloses. The hydrolytic pretreatment prior to pulping causes the solubilization of up to 83% of the initial hemicellulose in the range of experimental conditions tested. The lignin content is also reduced during pretreatment, and up to 12% of the initial lignin is solubilized. Experimental data show that both effects increase when the pretreatment severity parameter, $\log_{10}R_0$ rises. No significant changes in the cellulose content were observed as a function of the same parameter.

Soda-anthraquinone pulping at the optimal conditions produced pulps with kappa numbers ranging from 28.5 for non pretreated sample to 16.6 for the sample pretreated at the highest severity tested (231 °C and 5.5 min of residence time). Experimental data shows that the kappa number decreases when pretreatment severity rises. Chemical analysis of this pulp shows that the hemicellulose content of the fiber is not detectable by HPLC analysis. On the contrary, for the pulp prepared at the same pulping conditions but without pretreatment, the residual content of hemicellulose was 23%.

One drawback of the process is that the yield of cellulose also decreases with pretreatment. For the sample pretreated at the highest severity, the yield of cellulose after pulping was only 64% while it was 90% for the pulp prepared from the original softwood mixture. The DPv of $\alpha$-cellulose remaining in pulp is 300 and 450 respectively.

In general, this process decreases the kappa number of the cellulose pulp to typical values of extended delignification and allows the hemicellulose to be removed, thus improving the chemical purity of cellulose. Based on the kappa numbers obtained, the cellulose pulps prepared by the sequence pretreatment-pulping may be bleached by totally-chlorine-free sequences.

The purity of the cellulose increases as the pretreatment severity is increased and consequently, from the point of view of chemical composition, can be used as raw material in applications that require high purity cellulose with low DP. However, the yield of potential cellulose may decrease significantly depending on the severity at which the pretreatment is performed.

In future work additional pretreatments should be introduced in order to determine the mildest conditions which mantain the same degree of cellulose purity after pulping.

## NOTATION

| | |
|---|---|
| AA | active alkali expressed as NaOH (originally expressed as $Na_2O$) |
| AE | active alkali expressed as NaOH (originally expressed as $Na_2O$) |
| AQ | anthraquinone |
| CED | cupriethylenediamine hydroxide. |
| $DP_V$ | viscosity-average degree of polymerization of the α-cellulose fraction. |
| % DSB | percentage in Dry Solid (original lignocellulosic) Basis |
| ext. | extractives |
| H | H-factor [21,22] |
| n.d. | non detectable value by HPLC analysis |
| $R_0$ | severity factor [23] |
| t | time |
| T | temperature |
| TA | total alkali charge (originally expressed as NaOH) |
| w/w | weight to weight ratio |
| $[\eta]_{CED}$ | intrinsic viscosity |

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