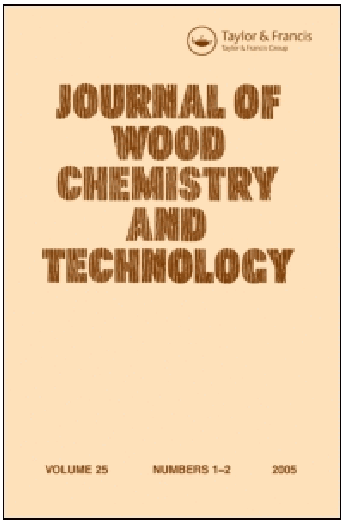

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Daniel Montané[a]; Xavier Farriol[a]; Joan Salvadó[a]; Paul Jollez[b]; Esteban Chornet[b]
[a] Departamet d'Enginyeria Química. ETSEQ, Universitat Rovira i Virgili, Tarragona, Catalunya, Spain [b] Departement de Génie Chimique, Université de Sherbrooke, Sherbrooke, Québec, Canada

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FRACTIONATION OF WHEAT STRAW BY STEAM-EXPLOSION PRETREATMENT AND ALKALI DELIGNIFICATION. CELLULOSE PULP AND BYPRODUCTS FROM HEMICELLULOSE AND LIGNIN

Daniel Montané , Xavier Farriol, Joan Salvadó
Departamet d'Enginyeria Química. ETSEQ. Universitat Rovira i Virgili
Carretera de Salou S/N. Tarragona, Catalunya. 43006 SPAIN

Paul Jollez and Esteban Chornet
Departement de Génie Chimique. Université de Sherbrooke
2500 Bd. Université. Sherbrooke, Québec. J1K-2R1 CANADA

ABSTRACT

The fractionation of wheat straw was studied using a two-stage process based on an hydrolytic pretreatment followed by alkali delignification. The hydrolytic pretreatment was performed by steam explosion. Straw was steamed at temperatures comprised between 205 and 230°C for 2 min. The steamed straw was washed with hot water to yield a solution rich in hemicellulose-derived mono- and oligosaccharides. The washed fiber was delignified by alkali at 160°C for 60 min using a NaOH load of 20%. The alkali-soluble lignin was recovered by filtration after acidification of the black liquor. The delignified pulp was screened and bleached to produce viscose-grade cellulose. The optimization of the pretreatment conditions led to the following results at a pretreatment severity of $\log(R_0) = 3.80$: yield of viscose-grade cellulose = 70% of the potential; lignin recovery = 70% of the Klason lignin present in the untreated straw; hemicellulose sugars = 55% of the potential, recovered as molasses.

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INTRODUCTION

Wheat (*Triticum aestivum*) straw is an agricultural byproduct that is not used as industrial raw material at a significant scale in developed regions like North America and Europe, which are two of the major wheat producing areas, despite the magnitude of the yearly production of straw. Although straw yield depends on the specific varieties harvested and is widely affected by agronomic and climatic factors, an average ratio of 1.3 kg of straw per kg of grain is found for the most common varieties.[1] As a rough estimation, about 125 million tons of wheat straw are produced yearly in North America and nearly 170 million tons in Europe.[2] These amounts are significant enough to consider wheat straw as a generic source of renewable materials, particularly for the production of chemical derivatives from cellulose and lignin.

Fractionation of biomass has been studied as an option for the simultaneous production of hemicellulose, lignin, and cellulose fractions with reasonable yield and purity. Several applications for cellulose and lignin obtained from fractionation processes have been investigated. Economical feasibility of these alternatives depends on the capacity of establishing an strategy for the simultaneous transformation of all the biomass-derived fractions into marketable products.[3,4] Accordingly, a detailed knowledge of the chemical composition and characteristics of the fractionation products is required in order to appraise the potential end uses of each fraction. Most fractionation processes are based on the use of a physicochemical pretreatment that increases the reactivity of the lignocellulosic structure, followed by one or more separation and purification stages to isolate products. Hydrolytic treatment of lignocellulosics by saturated steam or hot water (autohydrolysis), or with addition of small amounts of inorganic acids (prehydrolysis), has been widely studied as a method to weaken the lignocellulosic structure and increase its chemical reactivity and enzyme accessibility. A variety of processes aimed to the fractionation of biomass have been proposed and investigated during recent years based on this approach,[5-11] steam explosion among them. Steaming of lignocellulosics in batch digesters followed by flash decompression (explosion) was developed by Mason[12] for the production of hardboard in the process known as Masonite. Similar batch units and new continuous digesters have been used for the pretreatment stage in biomass fractionation processes.[13-17] From a chemical point of view steam-explosion does not differ from the rest of hydrolytic pretreatment methods. In fact, the flash pressure release at the end of the steaming period does not affect in any appreciable extent the chemical composition nor the polymer characteristics the substrate being treated. The changes in composition and molecular weight are only caused by the hydrolytic process.[18] Hydrolytic pretreatment at high temperature and short residence time is of interest for biomass fractionation, since high temperature favors hemicellulose solubilization, while a short residence time avoids much degradation of the solubilized oligomers and increases substantially the yield of the hemicellulose fraction recovered after washing.[19] Consequently, a treatment time as short as two or three minutes may be required in order to avoid excessive depolymerization and degradation of carbohydrates when steaming is performed at high temperature (i.e. above 190°C). Steam-explosion is suitable for studying the effect of the pretreatment in conditions of high temperature and short residence time: direct steaming allows a rapid rise to the desired reaction temperature, while the fast pressure release at the end of the steaming period gives way to instantaneous quenching of the products, thus avoiding the hydrolytic reactions to stretch out during cooling of the reactor.

Fractionation of wheat straw has been much less studied than wood fractionation despite the magnitude of the yearly production of straw. Works on wheat straw fractionation have been centered on the pretreatment by dilute acid hydrolysis[20] or autohydrolysis.[21-23] Complete fractionation sequences combined steam pretreatment at low temperature with organosolv delignification.[24,25] The aim of this work is to evaluate fractionation of wheat straw by a process sequence based on controlled autohydrolysis at high temperature followed by hemicellulose extraction and alkali delignification. The work has been carried out at the laboratory bench scale level, and has established the yield, chemical composition and molecular weight distribution of each fraction obtained.

EXPERIMENTAL

Wheat straw

A batch of 100 kg of wheat straw (*Triticum aestivum*) from the north-eastern

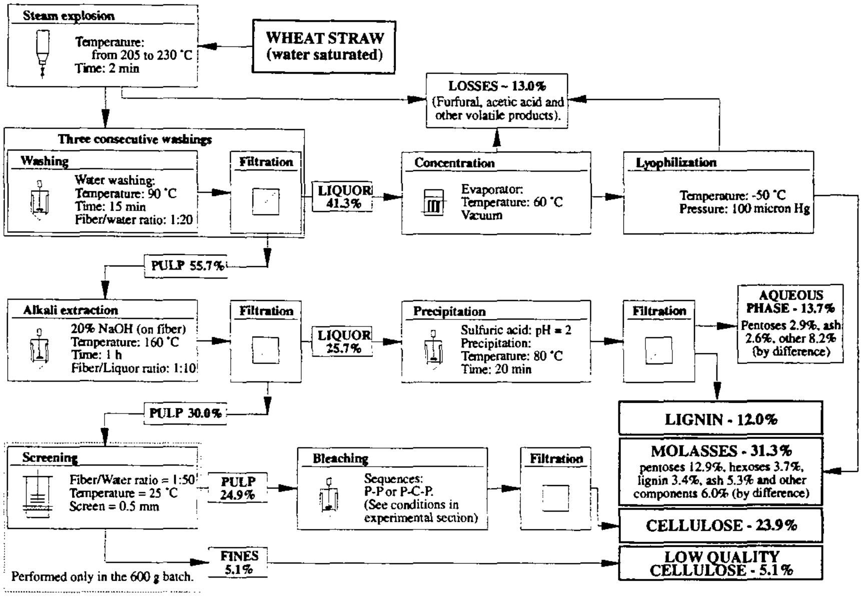

FIGURE 1. Flow diagram of the fractionation process and operational conditions used in each stage. Yields of the different fractions are indicated for a pretreatment severity of $\log(R_0) = 3.80$, and P-C-P bleaching.

region of Spain was used in the present study. The moisture content of the straw was 8% on reception. A representative sample of the batch was ground to 40 mesh and its chemical composition was established using the methods described in this section. Chemical composition is shown in Table 1.

Fractionation process

Wheat straw fractionation was performed following the procedure shown in in Figure 1, which includes the mass balances for the optimal pretreatment severity studied in this work. An amount of water-saturated straw equivalent to 100 g of dry straw was treated in each experiment by steam explosion in a 4.5 L

TABLE 1

Chemical Composition of the Batch of Wheat Straw.

Fraction	% dry straw basis (% DSB)
Ash	8.0
Ethanol/Toluene extractives	5.4
Hot water extractives[1]	6.2
Glucan (HPLC)	32.3
Xylan (HPLC)	20.5
Arabinan (HPLC)	3.1
Klason lignin[1]	17.1
Chlorite holocellulose[1]	64.1
α-cellulose[1]	33.7
α-cellulose DP_V	960

[1] Ash corrected.

batch reactor for 2 min at temperatures from 205 to 230°C. The depolymerized hemicellulose sugars were recovered from the exploded fiber by three successive washings with water at 90°C during 15 min, at a fiber/water ratio of 1/20. The resulting solution was concentrated under vacuum at 60°C in an evaporator (Büchi, R-151), frozen, and lyophilized at -50°C (Labconco freeze dryer 5).

The washed fiber was then delignified by alkali treatment at 160°C for 60 min using a fiber/liquor weight ratio of 1/10 and a NaOH load of 20%, based on the dry exploded fiber. These severe temperature/time conditions were used in order to reach a very low lignin content in the delignified cellulose. After removal of the remaining cellulose by filtration the black liquor was acidified to a pH of 2 at 80°C with sulfuric acid, and the precipitated lignin recovered by filtration. Lignin was then thoroughly washed with water until neutrality, air-dried at room temperature and stored for further analysis. Cellulose was washed with water several times until a colorless solution was obtained. Part of the cellulose was air-dried and analyzed for chemical composition, while the rest was stored at 5°C for further bleaching. In some of the experiments cellulose was refined in a domestic blender to achieve a complete defibration, and screened before bleaching in order to remove the fines. Defibration was carried out at 2% consistency during 90 s. Screening was performed with a 0.5 mm screen at a fiber/water ratio of 1/50.

Removal of the residual lignin in cellulose was attempted using two different bleaching sequences:

Two stage peroxide bleaching (P-P). A procedure based on hydrogen peroxide as bleaching agent was initially used for all the cellulose samples. Cellulose was submitted to two consecutive bleaching treatments at 60°C for 60 min using a pulp/liquor weight ratio of 1/10. Chemicals load on the bleaching liquor, expressed as weight % on the dry pulp, were 5% H_2O_2, 1% NaOH and 0.5% $MgSO_4$. After each stage, the pulp was filtered and thoroughly washed with distilled water.

Three stage P-C-P bleaching. An intermediate chlorination stage was included for the bleaching of some of the cellulose samples, due to the inadequate results obtained with the previous sequence. It has been demonstrated that the chlorination stage increases the efficiency and selectivity of the O-C-O and O-C-P bleaching processes.[26] Experimental conditions were: first stage (P: 60 min; 3% H_2O_2, 1% NaOH and 0.5% $MgSO_4$), second stage (C: 15 min; 1% Cl_2 and 2% HCl) and third stage (P: 60 min; 2% H_2O_2, 2% NaOH and 0.5% $MgSO_4$). In all stages a temperature of 60°C and a pulp/liquor weight ratio of 1/10 were employed. After each stage the pulp was filtered and thoroughly washed.

Analytical methods

The chemical composition of the native wheat straw, the pretreated fiber and the final cellulose samples were determined using the following standard methods: ASTM D 1102-84 for ash content; ASTM D 1111-84 for hot water extractives; modified ASTM D 1107-84 for ethanol/toluene extractives; TAPPI 223 cm-84 for pentosan. Lignin content was measured as Klason lignin (ASTM D 1106-84) or by the Kappa number method (TAPPI 236 os-76). Holocellulose was determined by sodium chlorite delignification,[27] and α-cellulose was measured on holocellulose following the TAPPI T-203 os-74 standard. The viscosity average degree of polymerization of α-cellulose (DP_V) was calculated from its intrinsic viscosity in CED, which was measured following the ISO 5351/1-1981 standard method.

Carbohydrate analyses in the raw material and the fiber samples during the stages of the process were performed by quantitative saccharification with sulfuric acid,[28] followed by HPLC measurement of the monosaccharides formed. After saccharification, an aliquot of the sample was neutralized by addition a fixed amount of solid $Ba(OH)_2$ and the mixture was homogenized using a magnetic stirrer. Final pH was adjusted to 6 with a solution of saturated $Ba(OH)_2$. The sample was centrifuged at 2000 rpm to remove barium sulfate, and an aliquot of 3 mL was filtered through a 0.45 µm filter and analyzed by HPLC using mannitol as internal standard. HPLC analyses were performed with a Bio-Rad Aminex HPX-87P column (300 x 7.8 mm) at 85°C using deionized water as solvent, which was delivered by a Gilson 302 pump at a flow of 0.7 mL/min. The volume of sample injected in each analysis was 50 µL. The eluted monosaccharides were detected with a Gilson 131 refractive index detector thermostated at 25°C.

Soluble products from hemicellulose depolymerization were quantified in the washings of the exploded fiber. Monosaccharides formed during the treatment were directly measured by HPLC using the aforementioned conditions. An aliquot of the washing liquor was hydrolyzed with 4% sulfuric acid at 120°C during 30 minutes, the monosaccharides formed were quantified by HPLC, and the equivalent amount of oligosaccharides and the ratio between monosaccharides and oligosaccharides present in the washing solution were then calculated. The molar mass distribution of the hemicellulose products was estimated by size exclusion chromatography using a Toyo Soda TSK-Gel 3000PW (600 x 7.5 mm) column, and a guard column (75 x 7.5 mm) of the same gel. The mobile phase was filtered and degassed 1.0 % acetic acid solution containing 0.02 % sodium azide and 0.05 M sodium nitrate to eliminate any electrostatic effects.[29] The solvent was delivered by a Waters 590 pump at a flow rate of 0.5 mL/min. A sample volume of 100 mL was injected using a Waters 712 WISP automated injector, and detection was carried out by a Waters 410 refractive index detector. Data acquisition and calculations were performed using the Waters Maxima 820 GPC software on a personal computer. Pullulans with molar masses ranging from 830,000 to 5800 (Shodex Co.), commercial oligomaltoses (DP 2 to 7), and xylose, were used as narrow standards to calibrate the system.

TABLE 2

Yield and Chemical Composition of the Wheat Straw Steamed and Washed, Expressed as Weight % of the Initial Dry Straw (% DSB), as a Function of the Pretreatment Severity, $\log(R_0)$

$\log(R_0)$	3.39	3.60	3.80	3.98	4.13
Fiber yield	70.3	60.5	55.7	54.9	53.8
Ash	3.1	3.0	2.7	3.1	3.4
Glucan (HPLC)	31.5	31.5	31.1	30.3	28.5
Pentosan	14.8	7.7	5.0	3.3	2.2
Klason lignin[1]	14.9	14.0	13.7	16.0	17.8
Other (by difference)	6.0	4.3	3.2	2.2	1.9
Chlorite Holocellulose[1]	51.5	43.1	37.5	35.7	34.2
α-cellulose[1]	31.6	31.2	30.0	27.7	22.9
α-cellulose DP_V	829	780	605	417	243

[1] Ash corrected.

Elemental composition of the lignin recovered by the fractionation process was measured using a Perkin Elmer 640 C analyzer. Lignin was analyzed for methoxyl and acetyl content, and a sample of each lignin was acetylated using the quantitative method proposed by Chum and co-workers.[30] The apparent (polystyrene-equivalent) molar mass distribution of the lignins were studied by gel permeation chromatography using the acetylated samples. Detailed procedures for the characterization of these lignin samples have been published elsewhere.[31]

RESULTS AND DISCUSSION

Steam explosion and pentosan recovery

Table 2 presents the evolution of the yield of fiber and its chemical composition as a function of the steam explosion severity, R_0, calculated by Equation 1. R_0 is an empirical parameter that combines the temperature and treatment time into a singe variable for the monitoring of the hydrolytic processing of lignocellulosic biomass.[32] All the values are expressed as weight % of the initial dry straw (% DSB). Fiber yield decreases from 70.3% DSB at $\log(R_0) = 3.39$ to 55.7% DSB at $\log(R_0) = 3.80$, and remains nearly constant at higher severity in the range here studied. A significant decrease in the ash content of the fiber, from 8.0% DSB in the original straw to an average value of 3.0% DSB in the exploded fiber, is observed, showing that much of the ash is solubilized along with the depolymerized hemicellulose during the washing stage.

Measurement of glucan in fiber by quantitative hydrolysis and HPLC analysis indicates that its content decreases slowly as the severity of the pretreatment is raised, from 31.5% DSB at $\log(R_0) = 3.39$ to 28.5% DSB at $\log(R_0) = 4.13$. The amount of α-cellulose in the fiber exhibits a much stronger variation, decreasing from 31.6% DSB to 22.9% DSB for the same severity change. Measurement of the viscosity-average degree of polymerization (DP_V) of the α-cellulose indicates that cellulose is continuously depolymerized as the pretreatment severity rises. Cellulose depolymerization produces low molecular weight oligomers that are soluble in the strong alkali solution used for the α-cellulose analysis, thus yielding an apparent loss of cellulose that is higher than that inferred from the measurement of the glucan content by HPLC. This phenomena has been previously observed in the treatment of hardwood species by steam explosion[33] and aqueous-phase processing.[32]

$$R_0 = \int_0^{t[\text{min}]} \exp\left(\frac{T[^\circ C] - 100}{14.75}\right) \cdot dt \qquad (1)$$

The polysaccharides of the hemicellulose fraction, mainly xylan, are depolymerized much faster than cellulose. The mixture of oligosaccharides that result from the depolymerization of hemicellulose are easily extracted from the exploded fiber by washing with hot water. The pentosan content of the exploded fiber decreases from 14.9% DSB at $\log(R_0) = 3.39$ to only 2.2% DSB at $\log(R_0) = 4.13$. Table 3 shows the yield and characteristics of the hemicellulose-derived products recovered in the washing solution. The optimum yield is located

TABLE 3

Pentosan Recovery (as Weight % of the Potential Pentosan in Straw), Number Average- (M_n) and Weight Average- (M_w) Molecular Weights of the Mixture of Mono- and Oligo-Saccharides, as a Function of the Pretreatment Severity, log(R_0)

log(R_0)	3.39	3.60	3.80	3.98	4.13
Recovered by washing	34.6	54.6	54.8	44.7	27.3
Monosaccharides	0.3	1.3	2.7	5.4	7.5
Oligosaccharides	34.3	53.3	52.1	39.3	19.8
% (Mono/Total)	0.9	2.4	4.9	12.1	27.5
Remaining in the fiber	62.7	32.6	21.2	14.0	9.3
Degraded (by difference)	2.7	12.8	24.0	41.3	63.4
Molar mass distribution					
M_n	361	499	422	274	127
M_w	11,032	54,704	1,413	830	400
Polydispersity	30.6	110.0	3.3	3.0	3.1

at a severity comprised between $\log(R_0) = 3.60$ and $\log(R_0) = 3.80$. At these severity values the yield is 55% of the potential pentosan, and a maximum recovery of 60% may be expected at the optimum severity. These results are in good agreement with those available for the pretreatment of *Populus tremuloides*[16] and sugar-cane bagasse[17] by steam explosion, and almond shells by aqueous-phase autohydrolysis.[9] It is possible to increase the pentosan recovery if the steam treatment is conducted under mild acidic conditions.[18]

The hemicellulose products present in the washing solution are mainly formed of a mixture of oligosaccharides, and even at the highest severity studied only 27.5% of the recovered product is found in its monomeric form. GPC chromatograms of the pentosan samples, shown in Figure 2, demonstrate that there is a wide distribution of oligomer chain lengths, although it tends to narrow as the treatment severity increases. A significant fraction of high molar mass species is found at a severity below $\log(R_0) = 3.80$, which results in very high values of M_w and polydispersity for the molar mass distribution, as shown in Table 3. The existence of such high molar mass oligomers has also been observed

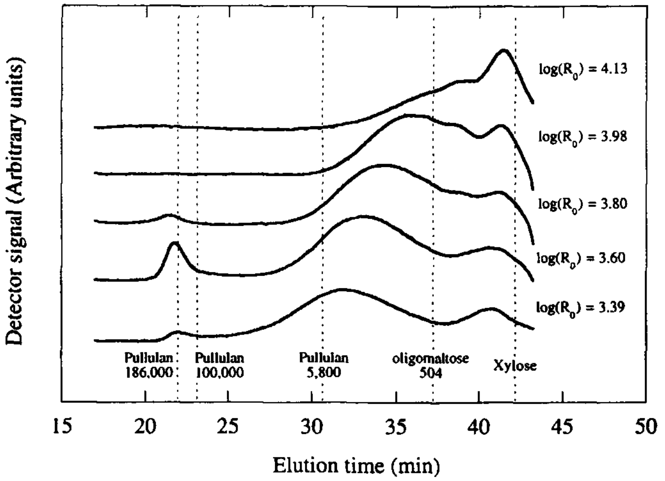

FIGURE 2. GPC chromatograms of the pentosan-derived products recovered in the washings of the exploded fiber as a function of the pretreatment severity, R_0. Elution times of known standards are included for comparison.

in the water processing of *Populus tremuloides*.[34] Data in Table 3 and Figure 2 indicate that the oligomers solubilized at low severity ($\log(R_0) = 3.39$) are of intermediate molar mass. Higher molar mass materials are removed as the severity increases to $\log(R_0) = 3.60$, being depolymerized to low molar mass oligomers and monomers in the liquid phase later on, if the reaction is extended to a higher severity. Monosaccharides undergo further degradation reactions as the reaction severity increases. The degraded fraction rises from 2.7% of the potential pentosan at $\log(R_0) = 3.39$ to 63.4% at $\log(R_0) = 4.13$.

Lignin is depolymerized during the steam treatment as this is performed at more drastic conditions. A significant fraction of the lignin present in the original straw is solubilized during the washing of the pretreated fiber with hot water.

Results in Table 2 show that at a severity up to $\log(R_0) = 3.80$ the Klason lignin content of the fiber decreases smoothly, from 17.1% DSB in the native

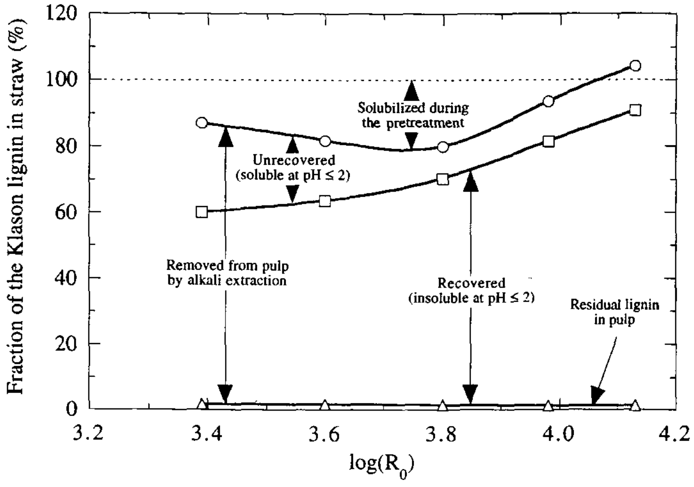

FIGURE 3. Lignin distribution among the different fractions obtained in the process as a function of the pretreatment severity, R_0.

straw to 13.7% DSB. At this point, nearly 20% of the initial Klason lignin has been solubilized and removed from the fiber during the washing stage. Beyond this pretreatment severity the content of Klason lignin of the fiber rises again, probably due to the formation of pseudo-lignin by condensation reactions involving the products from the hemicellulose degradation.[32,33] Consequently, the amount of Klason lignin that remains in the washed fiber is 17.8% DSB at $\log(R_0) = 4.13$, a value that is higher than the content in the native wheat straw (17.1% DSB). This behavior is well illustrated in Figure 3, where the distribution of the wheat straw lignin among the different fractions originated during the process is presented *vs.* the pretreatment severity.

Fiber delignification and lignin recovery

The yield of lignin recovered from the pulping liquor after acidification and vacuum filtering is shown in Figure 3 as a function of the steam pretreatment severity. Lignin yield continuously increases from 60.3% of the Klason lignin in the native straw at a steam treatment severity of $\log(R_0) = 3.39$, to a value of

TABLE 4

Lignin Composition as a Function of the Pretreatment Severity, $\log(R_0)$

$\log(R_0)$	3.39	3.60	3.80	3.98	4.13
Chemical composition[1]					
Ash content	0.02	0.02	0.07	0.15	0.27
Klason lignin	92.8	93.1	93.4	94.4	94.3
Residual pentosan	1.8	1.2	0.8	0.4	0.3
Other (by difference)	5.38	5.68	5.73	5.05	5.13
Carbon[2]	64.3	65.2	65.0	65.6	65.6
Hydrogen[2]	5.8	5.9	5.8	5.9	5.8
Nitrogen[2]	0.5	0.6	0.7	0.8	0.8
Oxygen (by difference)[2]	29.4	28.3	28.5	27.7	27.8
Molar Mass Averages					
M_n	4555	4815	4795	5563	4511
M_w	1277	1322	1460	1482	1206
$C_9H_aO_bN_c(OCH_3)_d(COCH_3)_e(OH)_e$					
Hydrogen	6.9	7.1	7.1	7.4	7.6
Oxygen	2.4	2.4	2.4	2.3	2.5
Nitrogen (x10)	0.7	0.8	0.9	1.0	0.9
Methoxyl	1.0	0.8	0.8	0.7	0.5
Acetyl (x100)	0.6	0.4	0.5	0.5	0.6
Total OH	0.9	1.0	1.0	0.1	0.9

[1] % of lignin. [2] % ash free lignin.

90.8% at $\log(R_0) = 4.13$. Elemental composition of the lignin samples, shown in Table 4, appears to be very similar, although there is a small increase in the carbon and nitrogen contents and a decrease in the oxygen content as the severity increases. The hydrogen content remains nearly constant in all the severity range studied. The recovered alkali lignins show very low ash contents, while the content of residual pentosan is 1.8% at the lowest severity studied and shows a smooth decrease to a value of 0.3% as the treatment severity increases to $\log(R_0) = 4.13$.

The molar mass distributions of the acetylated lignins are shown in Figure 4 as a function of the steam pretreatment severity. In this plot, the area under each distribution curve is proportional to the yield of lignin recovered in the process, and the molar mass scale indicates polystyrene-equivalent molar masses. The

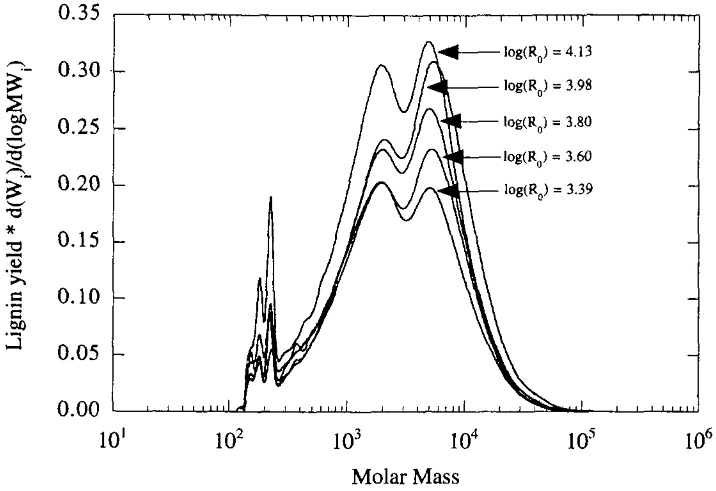

FIGURE 4. Molar mass distributions (polystyrene-equivalent) of the acetylated lignin samples as a function of the pretreatment severity, R_0.

weight– (M_w) and number– (M_n) molar mass averages of the acetylated lignin samples, calculated from the GPC chromatograms, are also listed in Table 4 as a function of the steam explosion pretreatment severity. M_w rises from 4555 at $\log(R_0) = 3.39$ to a maximum of 5663 at $\log(R_0) = 3.98$, from where it decreases to 4510 at the maximum severity studied. M_n presents an equivalent evolution, growing from 1277 at the lowest severity to a maximum of 1482 at $\log(R_0) = 3.98$, and decreasing to 1205 at $\log(R_0) = 4.13$.

Lignin C9 formulae are listed in Table 4, the more significant result being the rapid decrease in the number of methoxy groups as the pretreatment is performed at more severe conditions. A more detailed discussion of the characteristics of the lignin produced from wheat straw by this process has been published elsewhere.[31]

Cellulose characteristics and purification

The yields and compositions of cellulose obtained from the pretreated straw by alkali extraction are shown in Table 5. Bleachable-grade cellulose is obtained

TABLE 5

Chemical Composition of the Cellulose Pulp Obtained After Soda Pulping and After the Two Stage Hydrogen Peroxide Bleaching.

$\log(R_0)$	3.39	3.60	3.80	3.98	4.13
Delignified					
Yield[1]	35.3	30.1	30.0	25.0	19.5
Ash[2]	0.7	0.3	0.3	0.4	0.9
Pentosan[2]	15.2	7.0	3.4	3.1	1.7
Kappa number	11.0	11.1	10.1	8.7	8.8
Bleached (PP)					
Yield[1]	34.0	29.1	29.1	24.2	18.0
Ash[2]	0.2	0.1	0.2	0.4	0.5
Pentosan[2]	13.2	6.8	3.2	2.0	1.3
Kappa number	5.0	5.4	4.0	2.5	2.7
α-cellulose[2,3]	85.2	90.2	89.6	82.4	63.5
β-cellulose (by diff.)[2]	0.7	2.1	6.5	15.2	34.3
Cellulose DP_V	857	792	616	378	255

[1] *% of initial dry straw.* [2] *% of cellulose pulp.* [3] Ash corrected.

in all the margin of pretreatment severity studied, with kappa numbers decreasing from 11 at $\log(R_0) = 3.39$ to 8.8 at $\log(R_0) = 4.13$. The pentosan content of the pulp is also reduced. Characteristics of the pulps after bleaching by the two stage hydrogen peroxide sequence are also shown in Table 5. After pulping and bleaching the DP_V of the cellulose samples is similar to that found for the α-cellulose in the exploded pulp. The peroxide treatment substantially reduces the kappa number and the ash content of the pulps, but both are still high for a chemical application of the cellulose to be possible. Data from Table 5 suggests that cellulose obtained at a pretreatment severity around $\log(R_0) = 3.80$ may be suitable for viscose production if the process can be improved to yield a purer product (lower kappa number, pentosan, and ash contents). Cellulose with similar DP_V and composition obtained by steam explosion and alkali delignification of depithed sugar cane bagasse, has been shown to be suitable for the preparation of dissolving pulps.[17]

The removal of the fines fraction from the pulp and the use of a more efficient bleaching procedure were considered necessary in order to improve the

TABLE 6

Comparison Between the Chemical Composition of the Screened Pulp and the Fines Fraction After P-C-P Bleaching. (600 g Batch Prepared at $\log(R_0) = 3.80$).

Cellulose (P-C-P bleached)	Screened pulp	Fines
Yield[1]	23.9	5.1
Ash[2]	0.05	0.45
Pentosan[2]	4.0	4.3
Kappa number	1.0	2.1
α-cellulose[2,3]	92.8	75.1
β-cellulose (by diff.)[2]	3.00	19.84
cellulose DP_V	621	340

[1] % of initial dry straw. [2] % of cellulose pulp. [3] Ash corrected.

purity of cellulose. A batch of 600 g of wheat straw was treated by steam explosion at a severity of $\log(R_0) = 3.80$ and was delignified at the same conditions than those used in the previous experiments. The raw cellulose was screened to remove the fines and both fractions, screened cellulose and fines, were bleached separately using the P-C-P sequence described in the experimental section. The yield and composition of the screened cellulose and the fines fraction are shown in Table 6. The yield of cellulose after screening and bleaching was 23.9% DSB. This cellulose had a high purity, with an α-cellulose content of 92.8%, an ash content of only 0.05%, a kappa number of 1.0 and a DP_V of 621. The significant effect of the removal of the fines on cellulose quality is better appreciated when the chemical composition of this fraction is considered. The fines had an ash content of 0.45% and a kappa number of 2.1 after bleaching by the P-C-P sequence, both significantly higher than the values found for the screened cellulose. Cellulose in fines also exhibits a very poor quality, with an α-cellulose content of only 75.1% and a viscosity-average degree of polymerization of only 340 units. It is clear that the fines fraction is not suitable for chemical cellulose production. but, due to the increase in enzyme accessibility to the cellulose chains caused by the steam pretreatment and the alkali delignification, it may be a suitable feedstock for the production of glucose via enzymatic or acid hydrolysis.

Steam explosion at a moderate severity produces the rupture of a small fraction of the fibers in hardwoods, due to the stress generated on the cell structure by the sudden expansion that takes place during decompression, at the end of the steaming treatment. Massive fiber breakdown does not occur until a temperature higher than 230°C for at least 2 min is reached,[33] corresponding to a severity of $\log(R_0) = 4.13$. The high amount of fines produced during the steam explosion pretreatment of wheat straw at a moderate severity ($\log(R_0) = 3.80$), may be attributed to wheat straw anatomy. Wheat straw is formed by three main botanical components: internodes, nodes and leafs. Internodes account for 43 to 63% of the dry weight of the straw depending on the varieties, and show strong mechanical properties that allow their utilization in the manufacture of particleboard.[35] The nodes (3-4% of the straw), and specially the leaves, have very poor mechanical properties, and also higher ash and lower α-cellulose contents than the internodes.[1] Straw is formed by four main types of cells: 50% of bast and sclerenchyma fibers, 30% parenchyma, 15% epidermal cells and 5% vessels.[36] Bast fibers, which are mainly located in the internodes, are the principal source of fiber for cellulose pulps, while parenchyma and epidermal cells are very small and have no fibrous characteristics. The fines obtained in the process are probably a mixture of parenchyma and epidermal cells and fiber fragments that have been degraded mechanically from the most labile botanical components of straw, leafs and internodes, thus explaining the high ash and low α-cellulose contents observed for this fraction.

CONCLUSIONS

Processing of wheat straw by steam prehydrolysis/alkali delignification allows the fractionation of the three main polymers present in the lignocellulosic matrix. The yields of cellulose, lignin and hemicelluloses are strongly dependent on the severity of the steam pretreatment. Pentosans, recovered by washing of the exploded fiber, are obtained as a mixture of oligomers with only a minor presence of monomeric sugars. The average chain lengths of the oligomers continuously decrease as the pretreatment severity increases, enhancing also the amount of pentosan recovered as monosaccharides. A small fraction of high molecular weight oligomers is observed at a pretreatment severity below $\log(R_0) = 3.80$.

By adjusting the pretreatment severity it is feasible to produce viscose-grade cellulose by the steam explosion/alkali delignification process, although the inclusion of a screening stage is needed in order to remove the ash-rich fines fraction, which also has a low α-cellulose content. At a pretreatment severity of $\log(R_0) = 3.80$ a yield of 70% of viscose-grade cellulose, based on the α-cellulose content of wheat straw, is obtained. At this severity, 55% of the potential pentosans and 70% of the Klason lignin present in the initial wheat straw are also recovered as by-products.

The steam explosion pretreatment combined with alkali delignification is a well established process that allows the fractionation of lignocellulosic materials into polymeric fractions with reasonable yields and purity. Special care has to be taken in selecting the steam explosion conditions in order to avoid excessive degradation of the physical and chemical properties of the lignocellulosic polymers. The process is not totally selective, thus additional purification treatments of the polymer fractions obtained have to be considered before conversion to intermediate or final products. Such is the case for the production of viscose-grade cellulose, which we have shown requires a careful selection of the steam explosion conditions and the removal of the fines fraction before bleaching in order to obtain a good quality cellulose. The fines could be used as feedstock for hydrolysis to glucose.

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