Available online at www.sciencedirect.com

SCIENCE DIRECT®

Carbohydrate Research 340 (2005) 97–106

Carbohydrate
RESEARCH

Characteristics of degraded cellulose obtained from steam-exploded wheat straw

X. F. Sun,[a,c] F. Xu,[b] R. C. Sun,[b,c,*] P. Fowler[c] and M. S. Baird[d]

[a]*College of Forestry, The North-Western University of Agricultural and Forest Sciences and Technology, Yangling 712100, China*
[b]*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510641, China*
[c]*The BioComposites Centre, University of Wales, Bangor LL57 2UW, United Kingdom*
[d]*Department of Chemistry, University of Wales, Bangor LL57 2UW, United Kingdom*

Received 27 April 2004; accepted 27 October 2004
Available online 2 December 2004

Abstract—The isolation of cellulose from wheat straw was studied using a two-stage process based on steam explosion pre-treatment followed by alkaline peroxide post-treatment. Straw was steamed at 200 °C, 15 bar for 10 and 33 min, and 220 °C, 22 bar for 3, 5 and 8 min with a solid to liquid ratio of 2:1 (w/w) and 220 °C, 22 bar for 5 min with a solid to liquid ratio of 10:1, respectively. The steamed straw was washed with hot water to yield a solution rich in hemicelluloses-derived mono- and oligosaccharides and gave 61.3%, 60.2%, 66.2%, 63.1%, 60.3% and 61.3% of the straw residue, respectively. The washed fibre was delignified and bleached by 2% H_2O_2 at 50 °C for 5 h under pH 11.5, which yielded 34.9%, 32.6%, 40.0%, 36.9%, 30.9% and 36.1% (% dry wheat straw) of the cellulose preparation, respectively. The optimum cellulose yield (40.0%) was obtained when the steam explosion pre-treatment was performed at 220 °C, 22 bar for 3 min with a solid to liquid ratio of 2:1, in which the cellulose fraction obtained had a viscosity average degree of polymerisation of 587 and contained 14.6% hemicelluloses and 1.2% klason lignin. The steam explosion pre-treatment led to a significant loss in hemicelluloses and alkaline peroxide post-treatment resulted in substantial dissolution of lignin and an increase in cellulose crystallinity. The six isolated cellulose samples were further characterised by FT-IR and ^{13}C–CP/MAS NMR spectroscopy and thermal analysis.
© 2004 Elsevier Ltd. All rights reserved.

Keywords: Wheat straw; Steam explosion; Cellulose; Peroxide

---

1. Introduction

Since Mason[1] was granted for a patent in 1928 for a process in which wood chips or shavings were briefly treated with pressurised steam followed by a rapid release of pressure through a valve, steam explosion has become a well known method for separating lignocellulosic material into its main components: cellulose, lignin and hemicelluloses.[2–4] During the steam explosion, the significant amounts of hemicelluloses are partially hydrolysed and the some lignin is depolymerised, giving rise to sugars and phenolic compounds that are soluble in water. The hydrolysis of glycosidic linkages in hemicelluloses and the β-*O*-4 ether bonds in lignin are catalysed by acetic acid formed at high temperature from acetyl groups present in hemicelluloses (autohydrolysis). On the other hand, in autohydrolysis, the depolymerised lignin fragments remain in the proximity of condensation sites in the biomass matrix.[5] After a steam explosion, about 50% of the wood is obtained as a solid residue.[6] The residue consists mainly of cellulose and lignin, but also some hemicelluloses. The lignin and residual hemicelluloses may be removed by a subsequent alkali extraction, and can be recovered and used for the production of various chemicals. Some of the possible end products of steam-exploded wood are dissolving pulp, paper pulp, ethanol, xylitol, lactic acid and furfural or furfural derivatives.[4]

---

[*] Corresponding author at present address: The BioComposites Centre, University of Wales, Bangor LL57 2UW, United Kingdom. Tel.: +44 1248 370588; fax: +44 1248 370594; e-mail: bcs00a@bangor.ac.uk

0008-6215/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2004.10.022

Cellulose, the most abundant organic compound and a renewable resource, has incited researchers to work in the development of new production technologies for fuels, chemicals, and food. Physical treatments, such as crushing and grinding, steam and irradiation, have been proven to be effective in creating accessibility to chemicals and enzymes.[7] On the other hand, chemical treatments of lignocellulosics with NaOH, SO_2 or H_2SO_4 as well as impregnation and delignification agents have been studied in processes, for example, chemical and chemical–mechanical pulping and acid hydrolysis. Their effectiveness depends on cellulose swelling as well as on lignin softening and/or removal.[8] Although the steam explosion processes have been identified as physical processes, they are rather physico-chemical processes since two phenomena are involved in this pre-treatment: (a) mechanical action caused by the rapid pressure release; (b) chemical action resulting from autohydrolysis (i.e., hydrolytic attack achieved by the acetic acid formed during the steaming). These effects have combined with chemical impregnation to produce new ultra-high-yield chemimechanical pulps, which require less refining energy than conventional processes.[9] It has been reported that physico-chemical steam explosion pre-treatments improve digestion of the resulting residues[10] and shred the fibres into many individual fragments.[11] Furthermore, the cellulose is also depolymerised and defibrillated, and undergoes a change in its crystallinity and the resulting product is more susceptible to hydrolytic enzymes. Therefore, the process is generally followed by a fractionation step, such as alkaline extraction, to separate the main cellulose component.[12–14] It has also been reported that the steam-exploded pulps have different morphologies from those of pulps produced by the sulfite or kraft process. They show, for example, a higher porosity in the fibre fragments.[15] In particular, the processes of commercial pulps, such as sulfite and kraft, require extended cooking and bleaching operations as well as large amounts of chemicals. The steam-exploded lignocellulosics may be an interesting alternative, and the cellulose in lignocellulosics is relatively stable at the high temperature during steam explosion.[4]

In this work, the steam explosion process was used to separate the components of wheat straw. To achieve variations of cellulose structures and chemical compositions, six different steam explosion experiments, in which the time and temperature were varied according to factorial designs, were performed. The analysis of residues permits determination of the operating conditions leading to the hemicelluloses hydrolysis and lignin degradation. Therefore, we post-treated the residues with alkaline peroxide. The resulting cellulose-rich fibres were characterised by acid hydrolysis, nitrobenzene oxidation of associated lignins, thermal analysis, Fourier transform infrared (FT-IR) and carbon-13 cross polarisation magic angle spinning nuclear magnetic resonance (^{13}C–CP/MAS NMR) spectroscopy.

2. Results and discussion

2.1. Steam explosion and yield of degraded cellulose

The yield of both the insoluble residue recovered by filtration after washing with water, and the cellulose preparations isolated after alkaline peroxide post-treatment, are given in Table 1. Since the steam explosion resulted in the hydrolysis of the major part of the hemicelluloses and a small part of the lignin became soluble in the aqueous phase, a residue of α-cellulose and lignin remains. The lignin was significantly extracted with alkaline peroxide. The residual insoluble material after alkaline peroxide post-treatment contained predominantly cellulose with a small percentage of hemicelluloses and minor quantities of lignin. In all the experiments, the exploded material was very inhomogeneous and contained unexploded material, probably because wheat straw of industrial size was used.

As the data shown in Table 1, the yield of residue after the steam explosion ranged between 60.2% and 66.2%.

Table 1. The yield (% dry matter), intrinsic viscosity (η), the viscosity average DP (P) and molecular weight (M_w) of steam-exploded residues and the cellulosic preparations obtained by alkaline peroxide post-treatment of the corresponding steam exploded straw residues with 2% H_2O_2 at 50 °C for 5 h under pH 11.5, respectively

Sample no[a]	Yield (%)	η (mL/g)[b]	P[c]	M_w[d]
C_{1a}	61.3	482.3	1659.2	268,780
C_{2a}	60.2	421.5	1428.7	231,450
C_{3a}	66.2	411.5	1391.1	225,360
C_{4a}	63.1	403.4	1360.7	220,430
C_{5a}	60.3	250.3	801.1	129,780
C_{6a}	61.3	418.0	1415.5	229,310
C_{1b}	34.9	195.2	607.9	98,480
C_{2b}	32.6	175.6	540.5	87,570
C_{3b}	40.0	189.0	586.5	95,020
C_{4b}	36.9	173.8	543.4	86,570
C_{5b}	30.9	173.1	532.0	86,190
C_{6b}	36.1	192.5	598.6	96,970

[a] C_{1a}, C_{2a}, C_{3a}, C_{4a}, C_{5a} and C_{6a} represent the steam-exploded residues obtained at 200 °C, 15 bar with water to straw ratio (mL/g) 2:1 for 10 min (C_{1a}) and 33 min (C_{2a}), at 220 °C, 22 bar with water to straw ratio (mL/g) 2:1 for 3 min (C_{3a}), 5 min (C_{4a}) and 8 min (C_{5a}), and at 220 °C, 22 bar with water to straw ratio (mL/g) 10:1 for 5 min (C_{6a}), respectively, while the C_{1b}, C_{2b}, C_{3b}, C_{4b}, C_{5b} and C_{6b} represent the cellulosic preparations obtained by alkaline peroxide post-treatment of the corresponding steam-exploded residues with 2% H_2O_2 at 50 °C for 5 h under pH 11.5, respectively.

[b] Determined by British Standard Methods for determination of limiting viscosity number of cellulose in dilute solutions, Part 1. Cupri-ethylene-diamine (CED) method.

[c] Calculated by $P^{0.90} = 1.65[\eta]$, P represents the viscosity average DP (degree of polymerisation).

[d] Calculated by $P \times 162$.

The yield of cellulose after the alkaline peroxide post-treatment varied between 30.9% and 40.0%. An increase in steam pre-treatment time from 10 to 33 min at 200 °C/15 bar with water to straw ratio 2:1 resulted in a slight decrease of the residue from 61.3% (sample 1) to 60.2% (sample 2). Similarly, at 220 °C/22 bar with same water to straw ratio, an increasing steam pre-treatment period from 3 to 5 and to 8 min led to a drop of residual yield from 66.2% (sample 3) to 63.1% (sample 4) and to 60.3% (sample 5). It should be noted that during the steam explosion pre-treatment, the hemicellulosic polymers are depolymerised much faster than lignin and cellulose, yielding the residues rich in cellulose and remain lignin together with small amounts of survived hemicelluloses.

Post-treatment with alkaline peroxide yielded residue ranging between 30.9% and 40.0%, which consisted mainly of cellulose, and in most cases were lower than the α-cellulose content (39.0%) in wheat straw. This revealed that small amounts of cellulose were degraded or hydrolysed during the sequential two-stage treatments with steam explosion and alkaline peroxide. This is particularly true when the steam pre-treatment was performed in a longer period, since its content decreased from 34.9% to 32.6%, and from 40.0% to 36.9% and to 30.9% as the pre-treatment incubation time raised from 10 to 33 min at 200 °C/15 bar, and from 3 to 5 and to 8 min at 220 °C/22 bar, respectively. Similar results have been reported by Montane et al.[16] in the study of fractionation of wheat straw by steam explosion. The authors stated that cellulose is continuously depolymerised as the steam pre-treatment severity rises. Cellulose depolymerisation produces low molecular weight oligomers that are soluble in the alkaline peroxide solution, thus yielding an apparent loss of cellulose. This phenomenon has been previously observed in the treatment of hardwood species by steam explosion[11] and aqueous-phase processing.[7] Taken together, the two-stage treatments degraded 77.0–87.6 of the total hemicelluloses and 92.3–99.4% of the total original lignin (based on the content of residual hemicelluloses and lignin in alkaline peroxide post-treated residues in Tables 2 and 3). The current results suggested that the steam pre-treatment resulted in a significant hydrolysis of hemicelluloses and alkaline post-treatment led to a substantial degradation of lignin.

In all the experiments, the exploded material was very dark. These colour changes during the steam

Table 2. The content of neutral sugars (relative % sample, w/w) in the steam-exploded wheat straws and the cellulosic preparations obtained by alkaline peroxide post-treatment of the corresponding steam-exploded straw residues with 2% H_2O_2 at 50 °C for 5 h under pH 11.5, respectively

Sugars	Preparations[a]											
	C_{1a}	C_{1b}	C_{2a}	C_{2b}	C_{3a}	C_{3b}	C_{4a}	C_{4b}	C_{5a}	C_{5b}	C_{6a}	C_{6b}
Arabinose	1.0	0.5	0.4	0.2	0.8	0.3	0.4	0.8	0.8	0.3	1.0	0.4
Xylose	14.2	8.2	8.5	4.6	14.8	13.4	13.7	8.7	12.1	4.6	17.7	12.4
Mannose	1.9	1.2	1.6	0.1	1.5	0.6	0.7	0.6	0.7	0.4	0.7	0.6
Galactose	2.9	1.9	2.6	0.3	1.3	0.3	0.2	0.3	0.1	0.2	0.2	0.3
Glucose	80.1	89.3	87.0	94.7	81.6	85.4	85.1	89.6	86.2	94.5	80.4	86.3

[a] Corresponding to the preparations in Table 1.

Table 3. The content of lignin (% dry sample, w/w) and its phenolic compounds in the steam-exploded wheat straw residues and the cellulosic preparations obtained by alkaline peroxide post-treatment of the corresponding steam-exploded straw residues with 2% H_2O_2 at 50 °C for 5 h under pH 11.5, respectively

Phenolic acids and aldehydes	Preparations[a]											
	C_{1a}	C_{1b}	C_{2a}	C_{2b}	C_{3a}	C_{3b}	C_{4a}	C_{4b}	C_{5a}	C_{5b}	C_{6a}	C_{6b}
p-Hydroxybenzoic acid	0.25	0.16	0.28	0.10	0.13	0.08	0.15	0.09	0.23	0.11	0.16	0.10
p-Hydroxybenzaldehyde	0.38	0.10	0.35	0.03	0.17	0.02	0.18	0.03	0.28	0.04	0.19	0.04
Vanillic acid	0.25	0.051	0.27	0.04	0.11	0.02	0.10	0.03	0.32	0.06	0.11	0.05
Vanillin	2.11	0.39	2.12	0.13	1.42	0.12	1.56	0.14	1.93	0.18	1.60	0.18
Syringic acid	0.10	0.09	0.07	ND[b]	0.08	ND	0.07	0.02	0.11	0.04	0.05	0.04
Syringaldehyde	2.87	0.46	2.98	0.16	2.18	0.09	2.31	0.11	1.92	0.13	2.33	0.16
Acetovanillin	0.36	ND	0.45	0.12	0.23	0.02	0.22	0.05	0.25	0.06	0.28	0.09
Acetosyringone	0.12	ND	0.10	0.10	0.11	0.03	0.13	0.05	0.19	0.05	0.15	0.07
p-Coumaric acid	0.23	0.02	0.19	T[c]	0.10	0.02	0.05	ND	ND	0.03	0.08	0.06
Ferulic acid	0.19	0.07	0.19	0.06	0.07	T	0.03	ND	ND	0.06	0.03	0.05
Cinnamic acid	0.06	0.02	0.05	0.05	0.04	ND	0.03	0.06	0.07	0.04	0.05	0.06
Total	6.92	1.36	7.05	0.79	4.64	0.40	4.83	0.58	5.30	0.80	5.03	0.90
Content of klason lignin	23.41	2.91	24.12	1.52	22.50	1.21	23.09	1.63	24.81	1.92	23.83	2.18

[a] Corresponding to the preparations in Table 1.

[b] ND = not detected.

[c] T = trace.

pre-treatment could be resulted from the changes in the main cell wall components during the steam explosion at different conditions tested. According to the steam explosion pre-treatment experiments performed using large ships (8–12 mm) at mild pre-treatment conditions (190 °C, 4 and 8 min) in pine,[17] the results showed that a significant amount of hemicellulosic sugar remained unhydrolysed in the water-insoluble fibre. In such conditions lower colour variations in comparison to raw material could be observed. However, as the steam pre-treatment temperature was raised to 210 °C, almost all the hemicelluloses (more than 90%) were released from the larger particle size, and these samples showed a more dark and brownish appearance. These colour changes are probably related to the chemical breakdown of lignin and extractives. Alternatively, the appearance of brownish products in treated samples may be also resulted from the sugar degradation products that are produced at higher steam pre-treatment temperatures.[18]

The different behaviour of the cellulose and steam-exploded straw residue to steam explosion pre-treatment conditions was confirmed by the study of their physical properties, such as degree of polymerisation. The values for viscosity average degree of polymerisation (P) and the corresponding molecular weight of steam-exploded straw and cellulose (alkaline peroxide post-treated residue) are listed in Table 1. As can be seen, the η, P and M_w decreased constantly with increasing pre-treatment temperature and time until reaching a value of $\eta = 173.1$, $P = 532.0$ and $M_w = 86{,}190$. It is evident that the steam pre-treatment at 220 °C/22 bar for 8 min led to severe cellulose degradation. The current results were consistent with the studies on the cellulose obtained from steam-exploded aspen wood.[4] The authors reported that in the steam explosion at 180 and 190 °C, the molecular weight of the cellulose was not greatly affected by the time. At higher temperatures (200–220 °C), a severe decrease in molecular weight with increasing time was observed. In comparison, the much lower values of P and M_w in cellulose fractions (C_{1b-6b}) than in steam-exploded residues (C_{1a-6a}) were also due to a substantial degradation of lignin and residual hemicelluloses from the steam-exploded straw residues during the alkaline peroxide post-treatment. Briefly, the cellulose may normally survive during the steam pre-treatment for a short incubation time, such as at 220 °C/22 bar for 3 min. An exception is after very severe stream pre-treatment, for example, at 220 °C/22 bar for 8 min.

2.2. Content of hemicelluloses and composition of neutral sugars

The material obtained after steaming and further peroxide processing was hydrolysed with H_2SO_4, followed by quantification of monosaccharides by GC. Sugars other than glucose and xylose were present in hydrolysates but only in minor quantities. As the data shown in Table 2, six steam-exploded straw residues C_{1a-6a} had a relatively high residual amount of xylose (8.2–17.7%). In comparison, at the same steam explosion temperatures for a longer incubation time (C_{2a} and C_{5a}) the exploded material had a lower content of xylose (8.5% and 12.1%). An increase in glucose from 80.1% (C_{1a}) to 87.0% (C_{2a}) or from 81.6% (C_{3a}) to 85.1% (C_{4a}) and to 86.2% (C_{5a}) with an increment in steam pre-treatment time from 10 to 33 min at 200 °C/15 bar or from 3 to 5 and to 8 min at 220 °C/22 bar corresponded to the higher in cellulose content and lower in survived hemicelluloses in steam-exploded straw residue. Clearly, the residue after alkaline peroxide post-treatment was dominant in glucose (85.4–94.7%), resulting from cellulose, but still contained a noticeable amount of noncellulose sugars such as xylose (4.6–13.4%), galactose (0.2–1.9%), mannose (0.1–1.2%) and arabinose (0.2–0.8%). This resistance to extraction with alkaline peroxide under the condition used indicated that the hemicelluloses in the cell walls of wheat straw are tightly associated with cellulose, probably by hydrogen bonds, which can retain the hemicelluloses on the fibrils network during the peroxide post-treatment.[19] Interestingly, the hemicelluloses are significantly removed in samples C_{2b} and C_{5b} (content of noncellulose sugars 4.3–4.5%). This result is in agreement with Josefsson et al.[4] and Ibrahim and Glasser[20] who produced almost hemicelluloses-free cellulose from aspen wood and read oak under similar conditions. Further, as mentioned above, steam pre-treatment at high temperature led to severe cellulose degradation or structural modifications took place in cellulose during the steam explosion, leading to solubilisation of a fraction in alkaline peroxide post-treatment. Therefore, the cellulose content in C_{1b-6b} was underestimated. Consequently, the hemicelluloses degraded were overestimated as compared with their original content in wheat straw (38.7%). In short, the steam explosion pre-treatment with increasing time from 10 to 33 min at 200 °C/15 bar or from 3 to 5 and to 8 min at 220 °C/22 bar with water to straw ratio of 2:1, and sequential alkaline peroxide treatment under the condition given resulted in degradation of 20.0%, 20.8%, 12.3%, 15.1% and 29.1% of the original cellulose, respectively, from wheat straw exception for almost complete degradation of lignin and substantial hydrolysis of hemicelluloses.

2.3. Content of lignin and its phenolic composition

The content of lignin in steam-exploded straw residues (C_{1a-6a}) and the cellulosic preparations (C_{1b-6b}) was measured by its klason lignin, which is the material that is left after acid hydrolysis of the sample, since the acid hydrolysis mainly degrades polysaccharides to monosaccharides. The composition of the associated lignin was

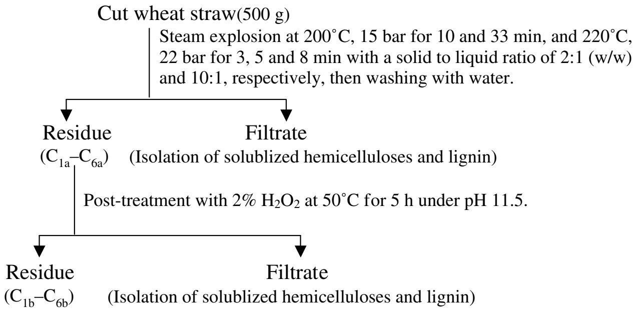

Figure 1. Scheme for fractionation of cellulose from steam-exploded wheat straw.

determined by alkaline nitrobenzene oxidation of the samples at 170 °C for 3 h, and their results are listed in Table 3. As can be seen, the content of lignin in $C_{1a–6a}$ ranged between 22.5% and 24.8%, which was higher than the lignin content in dry starting material (17.0%). At 200 °C/15 bar increasing pre-treatment time from 10 to 33 min resulted in a slight increment in lignin content from 23.4% (C_{1a}) to 24.1% (C_{2a}). Similar increasing trend of lignin was observed at 220 °C/22 bar. In this case the lignin content was increased from 22.5% (C_{3a}) to 23.1% (C_{4a}) and to 24.8% (C_{5a}) as the steam pre-treatment duration rose from 3 to 5 and to 8 min, respectively. The reason for this higher lignin content was undoubtedly due to the hydrolysis of substantial amounts of hemicelluloses during the steam pre-treatment, even though small amounts of lignin present in the middle lamella[8] were also degraded during the steam explosion, accounting for 11.2–12.3% of the total lignin. In addition, the residue recovered after a longer steam pre-treatment, was richer in lignin due to the increasing hemicellulose hydrolysis and lignin recondensation reactions (Fig. 1).

The data in Table 3 also showed that the six cellulose preparations ($C_{1b–6b}$) contained relatively low amounts of bound lignin, ranging between 1.2% and 2.9%. This rather low content of associated lignin in $C_{1b–6b}$ revealed that the α-benzyl ether linkages between lignin and hemicelluloses were significantly cleaved during the alkaline peroxide post-treatment under the condition given. Indeed, the sequential treatment with 2% H_2O_2 at 50 °C for 5 h under pH 11.5 led to degradation of 80.6–88.2% of the total lignin. Token together, the two-stage treatments degraded 92.3–99.4% of the original lignin from wheat straw. Thus, to obtain the maximum yields of each of the polymer fractions, would probably require a two-stage treatment cycle, with the removal of the bulk of the hemicelluloses and almost of the lignin to yield the cellulose with relatively high purity though at a low degree of polymerisation. The major products, obtained from alkaline nitrobenzene oxidation, were identified to be syringaldehyde and vanillin. This suggested that the lignin in the cell wall of wheat straw is composed mainly of noncondensed syringyl and guaiacyl units. Relatively, small amounts of *p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde, vanillic acid, syringic acid, acetovanillin, acetosyringone, *p*-coumaric acid and ferulic acid and trace of cinnamic acid were also detected in the nitrobenzene oxidation mixture.

2.4. FT-IR spectra

The FT-IR spectra of steam-exploded wheat straw residue C_{2a} (spectrum 1), C_{3a} (spectrum 2) and C_{5a} (spectrum 3) (Fig. 2) were very similar, indicating similar structure of the residues. They were characterised by a dominant O–H stretch band (ca. 3429 cm^{-1}) and a C–H band (ca. 2925 cm^{-1}) corresponding to the aliphatic moieties in lignin and polysaccharides (cellulose and survived hemicelluloses). A shoulder at 1726 cm^{-1} in the spectra 1 (C_{2a} obtained at 200 °C/15 bar for 33 min) and 2 (C_{2a} obtained at 220 °C/22 bar for 3 min) is attributed

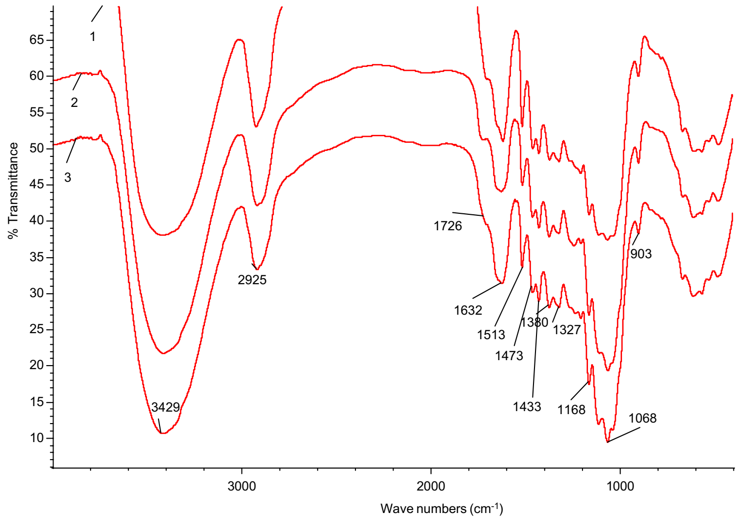

Figure 2. FT-IR spectra of steam-exploded wheat straw residue C_{2a} (spectrum 1), C_{3a} (spectrum 2) and C_{5a} (spectrum 3).

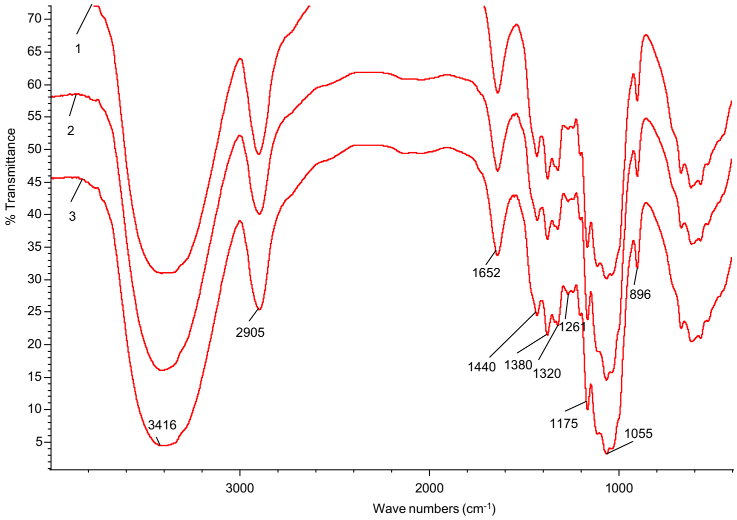

Figure 3. FT-IR spectra of cellulosic preparations C_{2b} (spectrum 1), C_{3b} (spectrum 2) and C_{5b} (spectrum 3) obtained by the alkaline peroxide post-treatment of the corresponding steam-exploded wheat straw samples.

to the acetyl and uronic ester groups of the hemicelluloses or from the ester linkage of carboxylic group of the ferulic and *p*-coumaric acids of lignin and/or hemicelluloses, whereas the almost absence of this signal in the spectra 3 indicated that the steam pre-treatment at 220 °C/22 bar for 8 min nearly cleaved this ester bond from the hemicelluloses and/or lignin. The band at $1632\,\mathrm{cm}^{-1}$ is due to the bending mode of the absorbed water. The aromatic C=C stretch from aromatic ring of lignin gives two peaks at 1513 and $1433\,\mathrm{cm}^{-1}$. The bands at 1473 and $1380\,\mathrm{cm}^{-1}$ reflect C–H symmetric and asymmetric deformations, respectively.[21] The absorbance at $1327\,\mathrm{cm}^{-1}$ is attributed to the C–C and C–O skeletal vibrations. The region of $1200–1000\,\mathrm{cm}^{-1}$ represents C–O stretch and deformation bands in cellulose, lignin and residual hemicelluloses. A small sharp band at $903\,\mathrm{cm}^{-1}$, which is indicative of the C-1 group frequency or ring frequency, is characteristic of β-glycosidic linkages between the sugar units.[22]

In the FT-IR spectra of cellulose preparations C_{2b}, C_{3b} and C_{5b} obtained by alkaline peroxide post-treatment of the corresponding steam-exploded residues, noticeable changes were observed at $1726\,\mathrm{cm}^{-1}$ and the bands relating to lignin aromatic ring vibrations at 1513 and $1433\,\mathrm{cm}^{-1}$. The disappearance of these bands revealed that lignin was more largely removed in comparison to polysaccharides during the peroxide post-treatment. The absorbances at 1440, 1380, 1320, 1261, 1175, 1055 and $896\,\mathrm{cm}^{-1}$ are associated with the typical values of cellulose (Fig. 3).

2.5. ^{13}C–CP/MAS NMR spectra

Figure 4 shows ^{13}C–CP/MAS NMR spectra of steam-exploded residue C_{1a} (spectrum a) and cellulosic fraction C_{1b} (spectrum b). The analysis of these spectra was conducted on the basis of previous work reported for wood and other plant systems[23,24] and the purified cellulose from wheat straw.[25] The resonances of cellulose occur at 105.1 or 105.2 ppm for C-1, at 83.0 or 83.6 and 88.0 or 88.4 ppm for C-4, and at 62.3 or 62.8 and 65.0 or 64.8 ppm for the C-6. The resonances of C-2, C-3 and C-5 overlap each other and appear at 72.2 and 74.7 or 74.1 ppm. In more detail, the peak at 88.0 or 88.4 ppm is assigned to crystalline cellulose and at 83.0 or 83.6 ppm to disordered cellulose. Similarly, the signal at 65.0 or 64.8 ppm relates to C-6 in crystalline cellulose and at 62.3 or 62.8 ppm to crystal surfaces or disordered cellulose. In comparison, an increase in intensity of the signals at 88.4 and 64.8 ppm in the spectra b indicated that post-treatment with alkaline peroxide would lead to an increment of crystallinity of the exploded material. In other words, the cellulose preparations obtained by alkaline peroxide post-treatment have a higher degree of crystallinity of cellulose than that of the steam-exploded straw residues, since there were no significant changes in crystallinity of cellulose during the various steam explosion conditions as reported by Fernandez-Bolaos and co-workers in the study of cellulose residue from steam-exploded olive stones.[5]

2.6. Thermal stability

Thermal analysis is convenient and reproducible, and is a useful method for characterising heterogeneous organic material. In particular, it is a valuable analytical method to investigate the physico-chemical properties of macromolecules such as cellulose. Figure 5 illustrates typical TGA/DSC curves of steam-exploded residues C_{1a} (Fig. 5a) and C_{2a} (Fig. 5b) obtained from wheat straw subjected to steam pre-treatment at 200 °C/15 bar for 10 and 33 min with water to straw ratio of 2:1

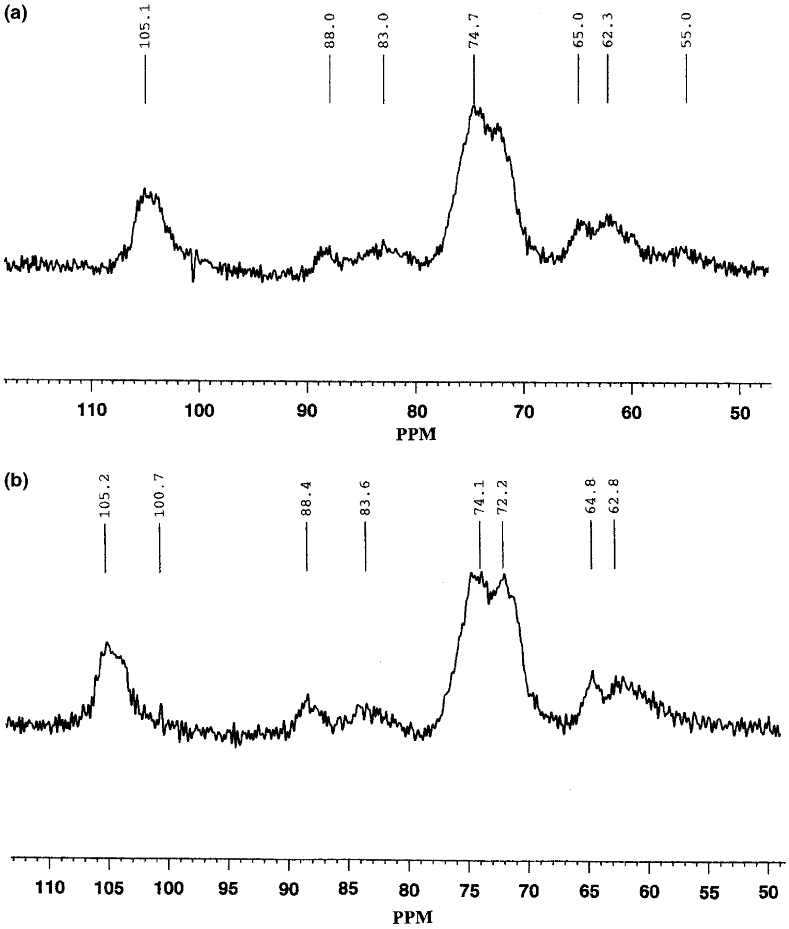

Figure 4. Solid-state ^{13}C NMR spectra of steam-exploded residue C_{1a} (spectrum a) and cellulosic fraction C_{1b} (spectrum b).

(mL/g), respectively. From the analysis of thermogravimetric curves it can be observed that decomposition of the two steam-exploded residues C_{1a} and C_{2a} takes place at about 260 °C. Similarly, when weight loss arrived at 50%, the temperature raised to about 330 °C for both of the residues. This phenomenon indicated that the two residues C_{1a} and C_{2a} had an equal thermal stability. In addition, the DSC thermogram of the two steam-exploded residues C_{1a} and C_{2a} showed a similar exothermic peak centred at 340 °C, indicating again an equal thermal stability.

The thermal decomposing patterns of the steam-exploded residue C_{5a} obtained at 220 °C/22 bar for 8 min and its corresponding cellulose preparation C_{5b} as well as cellulose fraction C_{4b} obtained by alkaline peroxide post-treatment, gave additional evidence to the relatively higher stability of the steam-exploded residue (Fig. 6). As shown in the figure, the TGA curves of steam-exploded residue C_{5a} and cellulose preparations C_{5b} or C_{4b} started to decompose at 272 and 234 °C, respectively. At 60% weight loss, the decomposition temperature of C_{5a} and C_{5b} or C_{4b} occurred at 287 and 257 °C, respectively. This implied that the steam-exploded residues had a higher thermal stability than the corresponding cellulose preparations. Further, the DSC thermogram of the steam-exploded residue C_{5a} gave a big exothermic peak at 283 °C, while the corresponding cellulose preparation C_{5b} exhibited only a small exothermic peak at 257 °C. Similar phenomenon was also observed in cellulose fraction C_{4b}, indicating again that the thermal stability of the steam-exploded residues was higher than that of the corresponding cellulose preparations obtained by post-treatment with alkaline peroxide. The reason for this higher thermal stability of the steam-exploded residue polymers was probably due to the generation of condensation substances between the polymers, leading to a more recalcitrant residue that requires higher temperature ranges for complete decomposition.

3. Conclusions

The results obtained in this study suggested that the steam explosion pre-treatment of wheat straw followed by alkaline peroxide post-treatment is a promising alternative separation process that allows the fractionation of lignocellulosic materials into polymeric fractions with

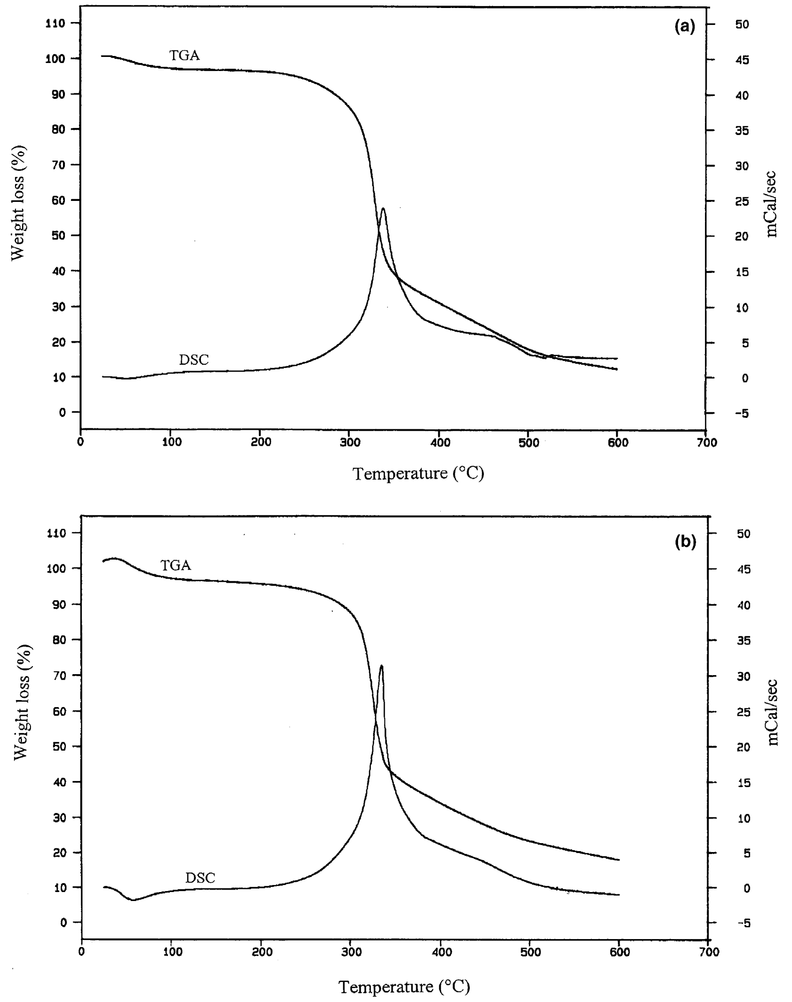

Figure 5. TGA/DSC curves of steam-exploded residues C_{1a} (a) and C_{2a} (b).

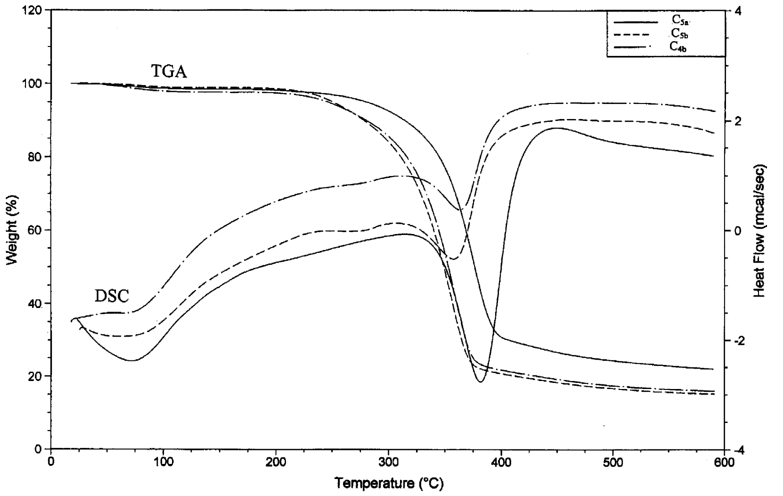

Figure 6. TGA/DSC curves of steam-exploded residue C_{5a} and cellulosic preparations C_{5b} and C_{4b}.

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 cellulosic polymers, since the yields of cellulose, lignin and hemicelluloses were strongly dependent on the conditions of the steam explosion pre-treatment, such as time and temperature in the explosions. It was found that the steam explosion pre-treatment degraded substantial amounts of hemicelluloses, while post-treatment with alkaline peroxide under the condition used removed significant amounts of lignin. Thus, to obtain the maximum yields of each of the polymer fractions, the straw would probably be required a two-stage treatment cycle, with the removal of the bulk of the hemicelluloses and almost of the lignin to yield the cellulose with relatively high purity. In addition, the cellulose obtained by steam pre-treatment and sequential alkaline peroxide post-treatment had a higher degree of crystallinity than that of the straw residues obtained by one stage of steam explosion. Furthermore, steam explosion produced cellulose products with different properties depending on treatment conditions. This led to the possibility of different chemical applications, for example, dissolving pulps, microcrystalline cellulose or powdered cellulose.

4. Experimental

4.1. Materials

Wheat straw (*Variety Riband*) was obtained from B Lloyd Co., Llangefni. It was dried in an oven for 16h and then cut into 2–3cm length. The composition (%, w/w) of the straw is cellulose 39.0%, hemicelluloses 38.7%, lignin 17.0%, ash 1.8% and wax 1.9% on a dry weight basis. The deviations of these contents from their respective means were all less than 6%. All chemicals used were of analytical grade.

4.2. Steam pre-treatment and alkaline peroxide post-treatment

The steam-explosion experiments were carried out in pilot-scale equipment with a 10L reactor (with a maximum operating pressure of 42kg/cm^2) fitted with a quick-opening ball valve. Six cooks were performed according to a factorial design. The temperature was kept at 200 and 220°C, and the heating time was varied between 3 and 33min. About 500g of dry straw was pretreated with steam explosion at 200°C, 15bar with water to straw ratio (mL/g) 2:1 for 10min (sample 1) and 33min (sample 2), at 220°C, 22bar with water to straw ratio (mL/g) 2:1 for 3min (sample 3), 5min (sample 4) and 8min (sample 5), and at 220°C, 22bar with water to straw ratio (mL/g) 10:1 for 5min (sample 6), respectively. When the desired temperature and treatment time was reached, a valve was opened and exploded, and the material was collected. The depolymerised hemicelluloses and their sugars as well as the degraded lignins were recovered from the exploded straw by washing with water at room temperature for 20min with a fibre to water ratio of 1g/20 mL. The residues (steam-exploded straw) recovered by filtration, were then thoroughly washed with distilled water at room temperature, oven-dried (60°C, 16h), and labelled as steam-exploded residues C_{1a}, C_{2a}, C_{3a}, C_{4a}, C_{5a} and C_{6a}, respectively. It should be noted that the exploded material, which was included in the analysis, was very inhomogeneous and contained unexploded material.

Each residue from steam explosion experiments 1 and 6 was then post-treated with 2% H_2O_2 to remove the depolymerised lignins and residual hemicelluloses, respectively. Before the treatment, the pH was adjusted to 11.5 with aqueous NaOH. The mixture was kept at 50°C for 5h. The fibre to liquor ratio was 1:20. After the post-treatment, the mixture was filtered and the residue (mainly cellulose) was washed with distilled water and ethanol until the filtrate was neutral, and dried in an oven at 60°C for 16h. These cellulose preparations were named as cellulose C_{1b}, C_{2b}, C_{3b}, C_{4b}, C_{5b} and C_{6b}, respectively. Figure 1 shows the fractionation of cellulose from the steam-exploded wheat straw. All experiments were performed at least in duplicate, with 5–7% standard error, and analyses were carried out at least three times for each of the sample. The standard errors or deviations of the analyses were observed to be lower than 6.8%. Yields of the steam-explode residues ($C_{1a–6a}$) and cellulose fractions ($C_{1b–6b}$) are given on a dry weight basis related to the starting wheat straw.

4.3. Characterisation of the steam-exploded residues and cellulose preparations

The content of residual hemicelluloses in $C_{1a–6a}$ and $C_{1b–6b}$ was detected by their sugar composition. The neutral sugar composition of the steam-exploded residues and cellulose preparations was determined by gas chromatography (GC) analysis of the corresponding alditol acetates after hydrolysis with 72% H_2SO_4 followed by dilution to 1M.[26] Klason lignin content in both residue and cellulose samples was determined according to Tappi method T 249cm-85. Alkaline nitrobenzene oxidation of associated lignin in $C_{1a–6a}$ and $C_{1b–6b}$ was performed at 170°C for 2.5h, and determined by high performance liquid chromatography (HPLC).[25] Method for measurement of the thermal stability of steam-exploded residues and cellulose preparations has been described in a previous paper.[27]

The average degrees of polymerisation (DP) and molecular weight of the steam-exploded residues and cellulose preparations were determined by British Standard Methods for determination of limiting viscosity number of cellulose in dilute solutions, Part 1. Cupri-ethylene-diamine (CED) method (BS 6306: Part 1: 1982). The viscosity average DP (degree of polymerisation) (P) of the steam-exploded residues and cellulose samples was estimated from their intrinsic viscosity [η]

in cupri-ethylene-diamine hydroxide (cuene) solution using the following equation:[28]

$$P^{0.90} = 1.65[\eta]/\mathrm{mL\,g^{-1}}$$

where P is an indeterminate average DP. Molecular weight of the steam-exploded residues and cellulosic preparations was then calculated from their P multiplying by 162, molecular weight of an anhydroglucose.

The FT-IR spectra of both six steam-exploded residues and six cellulose preparations were recorded from on a Nicolet-510 FT-IR spectrometer. Sample (~2 mg) was mixed and thoroughly ground with ~200 mg of KBr to reduce particle size and to obtain uniform dispersion of the sample in the disks. All the spectra were recorded in the absorbance mode from 4000 to 400 $\mathrm{cm^{-1}}$ for 32 scans at room temperature. The ^{13}C–CP/MAS NMR spectra were recorded on a Bruker MSL-300 spectrometer employing both Cross Polarisation and Magic Angle Spinning and each experiment was recorded at ambient temperature (293 ± 1 K). The spectrometer operated at 75.5 MHz. The speed of rotation was 5 kHz, the proton 90° pulse was 6 μs, the contact pulse 800 μs, and the delay between repetition at least 0.8 s. All samples were dried in an oven for 10 h at 50 °C before the spectra were recorded. All spectra were plotted without digital resolution enhancement.

Acknowledgements

The authors are grateful for the financial support of this research from the LINK program of the UK Ministry of Agriculture, Fisheries and Food, National Natural Science Foundation of China (No 30271061 and 30430550), Shaanxi and Guangdong Natural Science Foundation (No 2003k08-G18, 013034), and Ministry of Education China for a major project.

References

1. Mason, W. H. Apparatus for the process of explosion fibration of lignocellulose material. U.S. Patent 1,655,618, 1928.
2. Delong, E. A. Method of rendering lignin separable from cellulose and hemicelluloses in lignocellulosic material and the product so produced. Can. Patent 1,096,374, 1981.
3. Nguyen, Q. A. Continuous leaching of lignin or hemicellulose and lignin from steam pre-treated lignocellulosic particulate material. Can. Patent 1,322,366, 1989.
4. Josefsson, T.; Lennholm, H.; Gellerstedt, G. *Holzforschung* **2002**, *56*, 289.
5. Sun, X. F.; Xu, F.; Sun, R. C.; Fowler, P.; Baird, M. S. *Polym. Degrad. Stab.* **2004**, *86*, 245.
6. Josefsson, T.; Lennholm, H.; Gellerstedt, G. *Cellulose* **2001**, *8*, 289.
7. Overend, R. P.; Chornet, E. *Philos. Trans. R. Soc. London A* **1987**, *321*, 523.
8. Carrasco, F. *J. Wood Chem. Technol.* **1992**, *12*, 213.
9. Kokta, B. V. Process for preparing pulp and paper making. U.S. Patent 4,798,651, 1989.
10. Hohlberg, A. I.; Aguilera, J. M.; Agosin, E.; Martin, R. S. *Biomass* **1989**, *18*, 89.
11. Schultz, T. P.; Biermann, C. J.; McGinnis, G. D. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 344.
12. Fernandez-Bolanos, J.; Felizon, B.; Heredia, A.; Guillen, R.; Jimenez, A. *Bioresour. Technol.* **1999**, *68*, 121.
13. Beltrame, P. L.; Carniti, P.; Visciglio, A.; Focher, B.; Mazetti, A. *Bioresour. Technol.* **1992**, *39*, 165.
14. Martinez, J. M.; Granado, J. M.; Montane, D.; Salvado, J.; Farriol, X. *Bioresour. Technol.* **1995**, *52*, 59.
15. Samaranayake, G.; Li, X.; Glasser, W. G. *Holzforschung* **1994**, *48*, 69.
16. Montane, D.; Farriol, X.; Salvado, J.; Jollez, P.; Chornet, E. *J. Wood Chem. Technol.* **1998**, *18*, 171.
17. Ballesteros, I.; Oliva, J. M.; Navarro, A. A.; Gonzalez, A.; Carrasco, J.; Ballesteros, M. *Appl. Biochem. Biotechnol.* **2000**, *84*, 97.
18. Nergro, M. J.; Manzanares, P.; Oliva, J. M.; Ballesteros, I.; Ballesteros, M. *Biomass Bioenergy* **2003**, *25*, 301.
19. Mora, F.; Ruel, K.; Comtat, J.; Joseleu, J. P. *Holzforschung* **1986**, *40*, 85.
20. Ibrahim, M.; Glasser, W. G. *Bioresour. Technol.* **1999**, *70*, 181.
21. Cordeiro, N.; Neto, C. P.; Rocha, J.; Belgacem, M. N.; Grandini, A. *Holzforschung* **2002**, *56*, 135.
22. Geng, Z. C.; Sun, R. C.; Sun, X. F.; Lu, Q. *Polym. Degrad. Stab.* **2003**, *80*, 315.
23. Earl, W. L.; VanderHart, D. L. *Macromolecules* **1981**, *14*, 570.
24. Tang, H. R.; Wang, Y. L.; Belton, P. S. *Solid State NMR* **2000**, *15*, 239.
25. Sun, X. F.; Sun, R. C.; Su, Y. Q.; Sun, J. X. *J. Agric. Food Chem.* **2004**, *52*, 839.
26. Blakeney, A. B.; Harris, P. J.; Henry, R. J.; Stone, B. A. *Carbohydr. Res.* **1983**, *113*, 291.
27. Sun, J. X.; Sun, R. C.; Sun, X. F.; Su, Y. Q. *Carbohydr. Res.* **2004**, *339*, 291.
28. Evans, R.; Wallis, A. F. A. *J. Appl. Polym. Sci.* **1999**, *37*, 2331.