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Characteristics of degraded hemicellulosic polymers obtained from steam exploded wheat straw

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Abstract

The fractionation of wheat straw was studied using a two-stage process based on a steam explosion pre-treatment followed by alkaline peroxide post-treatment. Straw was steamed at temperatures comprised between 200 °C for 10 and 33 min and 220 °C for 3, 5, and 8 min. The steamed straw was washed with water to yield a solution rich in hemicelluloses-derived mono- and oligosaccharides (20.5–28.5%) together with small amounts of degraded hemicellulosic polymers (2.4–6.2%) and minor quantities of lignin (1.9–2.1%). The washed fibre was post-treated by 2% alkaline peroxide (pH 11.5) at 50 °C for 5 h. The alkali-soluble lignin (13.7–15.0%) and hemicelluloses (8.4–13.3%) were recovered by precipitation. The post-treatment was sufficient to remove lignin and survived hemicellulosic polymers and increase the brightness of the exploded straw significantly. The two-stage treatments together degraded 77.0–87.6 of the total original hemicelluloses and 92.3–99.4% of the total original lignin. This paper examined these two groups of six hemicellulosic polymer preparations degraded during the various steam explosion pre-treatments (H_{1a-6a}) and released during the sequential alkaline peroxide post-treatment (H_{1b-6b}). The effect of the most important variables in steam explosion pre-treatment (temperature, residence time, and water to straw ratio) on physico-chemical properties and structural features of the degraded hemicellulosic polymers were investigated. Thermoanalysis of these degraded hemicellulosic polymer fractions indicated that hemicellulose degradation products were also condensed to form more thermostable substrates during the steam explosion.

Keywords: Wheat straw; Steam explosion; Hemicellulosic polymers; Alkaline eroxide

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1. Introduction

Lignocellulosic materials such as wood and straw are renewable resources that can be directly or indirectly used for the production of biomolecules and commodity chemicals (Ghosh & Singh, 1993). In seeking low-cost sugar from lignocellulosics for use in biotechnological to chemicals, much attention has been given to so-called physical techniques such as grinding, milling, irradiation, and steam. Techniques involving an obvious addition of chemicals, such as in pulping or acid hydrolysis of biomass, are generally considered to be chemical processes. A more recent objective has been the fractionation of lignocellulosics to certain each of the major components in the maximum yield and purity. In this instance, the goals are those of extractive efficiency with minimum damage and loss of value. Thus it is hoped that it may be possible to obtain cellulose having characteristics allowing chemical substitution, lignin with thermoplastic and other polymer applications, and hemicelluloses for sucrochemistry (Overend & Chornet, 1987).

Pre-treatment of lignocellulosic materials is therefore essential for efficient utilization of renewable materials, and the best pre-treatment options are those in which both physical and chemical modification of the lignocellulosic

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materials are combined (Wood & Saddler, 1988). In this regard, high-pressure steaming, with rapid decompression (explosion), has been claimed as one of the most successful pre-treatment methods for fractionating lignocellulosic materials into their three major components and enhancing the susceptibility of cellulose to enzymatic attack (Excoffier, Toussaint, & Vignon, 1991). As early as 1928 Mason was granted a patent for a process in which wood chips or shavings were briefly treated with pressured steam followed by a rapid release of pressure (Mason, 1928). Since then, steam explosion has become a well know method for separating lignocellulosic materials or disrupting different biomass into the main components: cellulose, lignin, and hemicelluloses (Nguyen, 1989). The use of Mason process to effective separation of hemicelluloses and then lignin by successive extraction with water and alcohol solvents to leave a reasonable quality cellulose has been described in a patent by DeLong (1981). Autohydrolysis steam explosion has been recognized as a cost-effective method for pre-treating lignocellulosic biomass, because no addition of external catalyst is necessary. The most important operational conditions in steam-explosion pre-treatment are time, temperature, and chip size (Duff & Murray, 1996). Optimal conditions are defined as those in which the best substrate for hydrolysis is produced with the least material lost due to side reactions such as dehydration, and in which adequate carbohydrate linkages are disrupted by releasing the majority of the hemicelluloses into solution and leaving the cellulose fraction intact (Wu et al., 1999). The method is effective for a wide variety of plant biomass including wood (Dekker, Karageorge, & Wallis, 1987; Emmel, Mathias, Wypych, & Ramos, 2003; Ramos, Breuil, Kushner, & Saddler, 1992) and agricultural residues such as cereal straw (Tanaka & Matsuno, 1990).

It is generally agreed that the steam process is basically one of autohydrolysis because of the naturally acid conditions and the influence of the water and steam (Korte, Offermann, & Puls, 1991). The chemical changes which take place during steam explosion in the three main constituents of lignocellulosics (hemicelluloses, cellulose, and lignin) are very much dependent on the temperature and the time at temperature. The hemicelluloses are hydrolysed to soluble sugars by the organic acids, mainly acetic acid derived from the acetylated hemicelluloses in straw. In other words, the acetyl groups in the hemicelluloses are cleaved, forming acetic acid. The pH during steam explosion is kept low (pH 3–4) and much of the hemicelluloses are degraded. However, under more drastic conditions of higher temperature or longer incubation time, the solubilized hemicelluloses undergo a series of secondary reactions to form furfural and hydroxymethyl furfural. The reactive precursor besides undergoing self-polymerization can participate in condensation reactions with lignin (Chua & Wayman, 1979). Studies on birchwood by Puls, Poutanen, Korner, and Viikari (1985) indicated that 200 °C steaming temperature represents an optimum at a given incubation time of 10 min to achieve the recovery of 17% hemicellulose sugars in form of monomers to oligomers. Based on the studies in the rate of deacetylation under prehydrolysis conditions of birchwood, Maloney, Chapmann, and Baker (1985) revealed that a preferential removal of acetyl only took place at lower temperature between 100 and 130 °C, whereas the removal rates of xylan and acetyl nearly seemed equal at higher temperatures between 150 and 170 °C.

Studies on the steam explosion of wood have centred mainly on lignin fraction, for example, in the production of oxyaromatic compounds via thermal or catalytic depolymerization (Montane, Farriol, Salvado, Jollez, & Chornet, 1998), and the cellulose fraction, as in the case of prehydrolysis pulping and lately as a possible pre-treatment before enzyme saccharification of celluloses (Ramos et al., 1992). Thus so far there has been very little comprehensive work with regard to the effect of steaming on the hemicelluloses, particularly on non-mono- and non-oligosaccharides polymers degraded during the steam explosion. This paper concerns the hemicelluloses and is focused on the maximum recovery of the constitutive polymeric hemicelluloses for specific end uses. Both the hemicellulose liquors rich in pentoses and hemicellulosic polymers rich in xylan can readily become the raw material for a variety of chemicals among which, furfural and xylitol are prominent examples. The purpose of this present work was, therefore, to isolate and characterize the hemicelluloses degraded during the various steam explosion processes and the residual hemicelluloses surviving from the steam pre-treatment with a view to elucidating their physicochemical properties. The degraded hemicellulosic preparations were characterised using both the degradation methods such as acid hydrolysis and thermal analysis, and non-destructive techniques, e.g. Fourier transform infrared (FT-IR), carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR), and gel permeation chromatography (GPC). In addition, it is hoped that such characterization would provide further information on the utilization of the degraded hemicelluloses, which represent a potential source of renewable sugar and other chemicals.

2. Experimental

2.1. Materials

Wheat straw (*Variety Riband*) was obtained from B Lloyd Co., Llangefni. It was dried in an oven for 16 h and then cut into 2–3 cm length. The mean 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.

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

The steam-explosion experiments were carried out in pilot-scale equipment with a 10-litre reactor (with a maximum operating pressure of 42 kg/cm^2) fitted with a quick-opening ball valve. About 500 g of dry straw was pre-treated with steam explosion at 200 °C, 15 bar with water to straw ratio (ml/g) 2:1 for 10 min (sample 1) and 33 min (sample 2), at 220 °C, 22 bar with water to straw ratio (ml/g) 2:1 for 3 min (sample 3), 5 min (sample 4), and 8 min (sample 5), and at 220 °C, 22 bar with water to straw ratio (ml/g) 10:1 for 5 min (sample 6), respectively. The depolymerized hemicelluloses and their sugars were recovered from the exploded fibre by washing with water at room temperature for 20 min with a fibre to water ratio of 1 g/20 ml. The resulting solution was concentrated under vacuum at 50 °C in an evaporator. The degraded hemicellulosic polymers were isolated from the concentrated hydrolysates by precipitation with three volumes of 95% ethanol (20 °C, 5 h). The degraded hemicellulosic polymers recovered were then thoroughly washed with 70% ethanol, air-dried, and labelled as hemicellulosic preparations H_{1a}, H_{2a}, H_{3a}, H_{4a}, H_{5a}, and H_{6a}, respectively.

The insoluble material remained after washing with water was then post-treated with 2% H_2O_2 using a fibre to liquor ratio of 1 g/20 ml to remove the depolymerised lignins and residual hemicelluloses, respectively. Before the post-treatment, the pH was adjusted to 11.5 with aqueous NaOH. The mixture was kept at 50 °C for 5 h. After the treatment, the pH was 12–12.5. The mixture was filtered and the residue rich in cellulose was washed with water and ethanol until the filtrate was neutral, and dried in an oven at 60 °C for 16 h. The combined solutions were neutralized to pH 5.5 with 6 M HCl, evaporated at reduced pressure to remove ethanol, and concentrated. The hemicelluloses were then precipitated from the pooled solution with three volumes of 95% ethanol (20 °C, 5 h). The precipitate was filtered, washed with 70% ethanol, and air-dried. These hemicellulosic preparations released during the alkaline peroxide post-treatment were named as hemicelluloses H_{1b}, H_{2b}, H_{3b}, H_{4b}, H_{5b}, and H_{6b}, respectively. Fig. 1 gives the fractionation sequence of the degraded hemicelluloses. All experiments were performed at least in duplicate, and analyses were carried out at least three times for each of the sample. Yields of the degraded hemicelluloses are given on a dry weight basis related to the starting wheat straw.

2.3. Characterization of the degraded hemicellulosic preparations

The content of neutral sugars in isolated hemicellulosic polymer preparations was determined by analysis with trifluoroaetic acid (TFA) hydrolysis (2 M TFA at 120 °C for 2 h) prior to alditol-acetate derivatization and gas chromatography (GC) (Blakeney, Harris, Henry, & Stone, 1983). Uronic acid content was determined by the automated colorimetric *m*-hydroxydiphenyl assay (Blumenkrantz & Asboe-Hansen, 1973). Methods for measurement of the hemicellulosic molecular weights, thermal analysis, and determination of chemical composition of phenolic acids

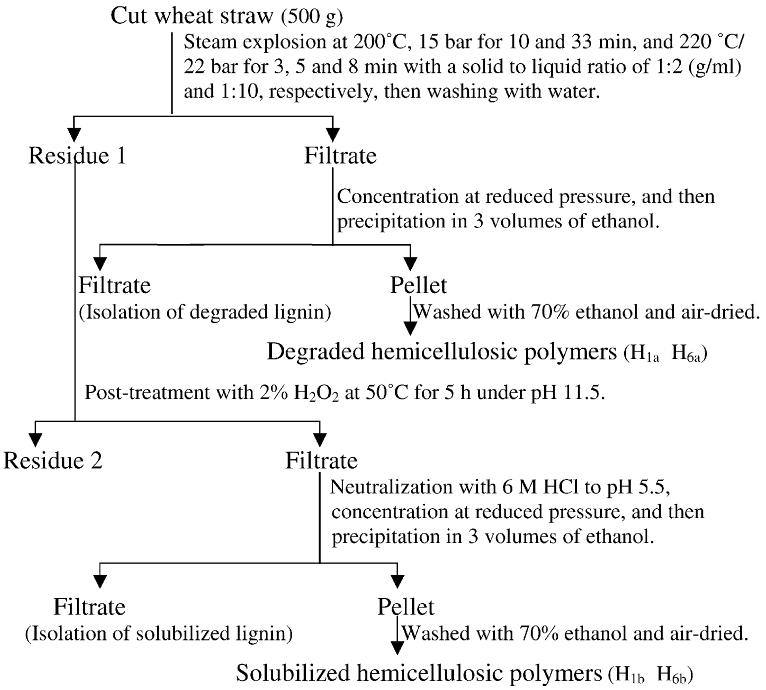

Fig. 1. Scheme for fractionation of degraded hemicellulosic polymers from steam exploded wheat straw.

and aldehydes liberated from alkaline nitrobenzene oxidation of the lignins associated in hemicellulosic fractions have been described in previously papers (Lawther, Sun, & Banks, 1995; Sun, Lawther, & Banks, 1996). Klason lignin content in hemicellulosic samples was determined according to Tappi method T 249 cm-85. FT-IR spectra were obtained on an FT-IR spectrophotometer (Nicolet 750) using a KBr disc containing 1% finely ground samples. The solution-state ^{1}H and ^{13}C-NMR spectra were obtained on a Bruker MSL-300 spectrometer at 300 and 74.5 MHz. ^{1}H NMR spectrum was recorded at 25 °C from 20 mg of sample dissolved in 1.0 ml D_2O. The ^{13}C-NMR spectrum was recorded at 25 °C from 80 mg of sample dissolved in 1.0 ml D_2O after 26,000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width and a 0.85 s delay time between scans were used.

3. Results and discussion

3.1. Steam explosion and yield of degraded and survived hemicellulosic polymers

The steam explosion process was used to separate the components of wheat straw. Six samples of steam explosions were performed, where the time and temperature were varied according to factorial designs. In all the experiments, the exploded materials was very inhomogeneous and contained unexploded material, probably because industrial grade of wheat straw was used. Information related to the yields of hemicelluloses and lignin degraded during the steam explosion pre-treatment and released during the alkaline peroxide post-treatment, and steam exploded and the post-treated residues is given in Table 1. All the values are expressed as weight% of the initial dry straw. Here the yield after the steam explosion, which varies between 60.2 and 66.2%, can be followed. The yield after the alkaline peroxide post-treatment varies 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 (ml/g) 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 6). No significant differences in the yield of the steam exploded residues were observed at 220 °C/22 bar with water to straw ratio between 2:1 and 10:1, as shown by their yields of 63.1% (sample 4) and 61.3% (sample 5). These steam exploded residues consisted mainly of cellulose, most of the lignin, and small amounts of survived hemicellulosic polymers (data not shown). It should be noted that small amounts of lignin degraded during the steam explosion was solubilized by washing the pre-treated straw with water, which yielded 1.9–2.1% of the starting straw, corresponding to 11.2–12.4% of the total original lignin in wheat straw.

During the steam explosion, the hemicellulosic polymers, mainly arabinoxylans, are depolymerized much faster than lignin and cellulose. As the data shown in Table 1, the yield of oligo- and monosaccharides produced during steam explosion pre-treatment ranged between 20.5 and 28.5%, which corresponded to 53.0–73.6% of the total original hemicelluloses. Obviously, the yield of oligo- and monosaccharides increased with an increment in steam incubation time and decreased when the water to straw ratio rose,

Table 1
The yield of hemicelluloses and lignin (% dry matter) degraded and/or solubilized during the steam explosion pre-treatment of wheat straw at various conditions and post-treatment with 2% H_2O_2 at 50 °C for 5 h under pH 11.5

Fraction	Sample[a]					
	1	2	3	4	5	6
Steam explosion pre-treatment						
Hemicelluloses degraded during the steam explosion pre-treatment and obtained by precipitation in ethanol[b]	6.2	2.4	4.8	4.2	3.6	4.4
Oligo- and monosaccharides produced during steam explosion pre-treatment[c]	20.5	28.5	21.1	25.1	26.8	22.5
Lignin degraded during the steam explosion pre-treatment[b]	2.0	1.9	2.0	2.1	2.0	2.1
Residue of steam exploded wheat straw (% dry starting matter)	61.3	60.2	66.2	63.1	60.3	61.3
Alkaline peroxide post-treatment						
Hemicelluloses solubilized in alkaline peroxide post-treatment[d]	13.3	11.8	8.4	9.2	13.3	10.3
Lignin solubilized in alkaline peroxide post-treatment[d]	13.7	15.0	14.7	14.8	14.9	14.8
Post-treated residue (α-cellulose)	34.9	32.6	40.0	36.9	30.9	36.1

[a] Represent for the samples pre-treated with steam explosion at 200 °C/15 bar with water to straw ratio (ml/g) 2:1 for 10 min (sample 1) and 33 min (sample 2), at 220 °C/22 bar with water to straw ratio (ml/g) 2:1 for 3 min (sample 3), 5 min (sample 4), and 8 min (sample 5), and at 220 °C/22 bar with water to straw ratio (ml/g) 10:1 for 5 min (sample 6).

[b] Represent for hemicellulosic polymer and lignin fractions degraded during the steam explosion pre-treatment.

[c] Represent for the hemicellulosic degradation products which are still solubilized in the supernatant after precipitation of the hemicelluloses in three volumes of ethanol, calculated by total hemicelluloses (38.7%) − (hemicellulosic polymers degraded during steam explosion pre-treatment obtained by precipitation in ethanol + hemicelluloses in pre-treated residues).

[d] Represent for hemicellulosic polymer and lignin preparation solubilized during the alkaline peroxide post-treatment.

indicating that an extension of steam pre-treatment time produced an increase of depolymerization of the hemicelluloses. Subsequently, the hemicellulosic polymers degraded during the steam explosion pre-treatment and obtained by precipitation in ethanol accounted for only small amounts of the total hemicelluloses in wheat straw, 2.4–6.2%, and they decreased from 6.2 to 2.4%, and from 4.8 to 4.2 and to 3.6% as the pre-treatment time increased 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. In contrast, at 220 °C/22 bar an increasing water to straw ratio from 2:1 to 10:1 resulted in a slight growth of degraded hemicellulosic polymers from 4.2 to 4.4%.

Historically, steam pre-treatment regimes have been optimised for improving digestibility of the cellulose component, and consequently, did not make efficient use of the hemicellulose component. More recently, with the recognition that complete utilization of the entire substrate will be required for improved process economics, pre-treatment strategies have focused both on cellulose hydrolysability and recovery of hemicelluloses and lignin. This has been accomplished through the use of less sever, single-stage pre-treatment and/or two-stage pre-treatment processes, which facilities efforts to optimise both hemicellulose and lignin recovery and cellulose treatment (Robinson, Keating, Mansfield, & Saddler, 2003). In this study, the recovery of degraded lignin and survived hemicelluloses from the steam pre-treated straw was performed by alkaline peroxide post-treatment (2% H_2O_2, 50 °C, 5 h, pH 11.5). As the data given in Table 1, the post-treatment released 8.4–13.3% degraded hemicellulosic polymers and 13.7–15.0% lignin, corresponding to 21.7–34.4% of the total original hemicelluloses and 80.6–88.2% of the total lignin from wheat straw. An increasing steam pre-treatment time from 3 to 5 and to 8 min at 220 °C/22 bar resulted in an increment in the yield of hemicelluloses from 8.4 to 9.2 and to 13.3% and lignin from 14.7 to 14.8 and to 14.9%, respectively. However, at 200 °C/15 bar increasing pre-treatment period from 10 to 33 min led to a growth of lignin from 13.7 to 15.0%, but a decrease of hemicelluloses from 13.3 to 11.8%. The reason for this decrease in hemicelluloses was undoubtedly due to a significant hydrolysis of hemicelluloses (28.5%) during the steam pre-treatment for a longer period (33 min). 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 post-treated residues, data not shown). 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.

After alkaline peroxide post-treatment, the yield of residue ranged between 30.9 and 40.0%, which in most cases were lower than the cellulose content (39.0%) in wheat straw, with about 2.5–14.6 and 1.5–2.9% of the substrate still present as hemicelluloses and lignin, respectively. 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. (1998) in the study of fractionation of wheat straw by steam explosion. The authors demonstrated that cellulose is continuously depolymerised as the steam pre-treatment severity rises. Cellulose depolymerization 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 (Schultz, Blermann, & Mcginnis, 1983) and aqueous-phase processing (Overend & Chornet, 1987).

In all the experiments, the exploded material was very dark. These colour changes during the steam pre-treatment could be corrected 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 (Ballesteros et al., 2000), the results showed that a significant amount of hemicellulosic sugar remained unhydrolysed in the water-insoluble fibre. The recovery yield of hemicelluloses in the steam treated residue calculated on the basis of hemicelluloses in untreated pine was 37.3 and 45.8% for 4 and 8 min. 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 related to ‘pseudo-melanoidins’ formation from sugar degradation products that are produced at higher steam pre-treatment temperatures (Nergro, Manzanares, Oliva, Ballesteros, & Ballesteros, 2003). Interestingly, with alkaline peroxide post-treatment, the brightness was significant increased as shown by the white post-treated residues. This implied that the alkaline peroxide post-treatment had also a good bleachability.

3.2. Sugar composition

As discussed above, various trends were observed with regard to degradation of hemicelluloses, lignin, and cellulose during the steam pre-treatments. These changes in chemical composition were basically a result of xylan

Table 2
The content of neutral sugars (relative % hemicellulosic sample, w/w) and uronic acids (% hemicellulosic sample, w/w) in the hemicellulosic polymer fractions

Sugars	Hemicellulosic fractions[a]											
	H_{1a}	H_{1b}	H_{2a}	H_{2b}	H_{3a}	H_{3b}	H_{4a}	H_{4b}	H_{5a}	H_{5b}	H_{6a}	H_{6b}
Arabinose	4.0	4.8	7.5	6.6	5.8	9.2	4.5	6.1	6.6	5.5	3.9	10.9
Xylose	69.2	76.3	39.9	54.2	64.7	70.3	28.6	47.8	26.2	39.9	47.5	69.3
Mannose	2.9	0.7	11.0	3.3	3.6	1.2	10.4	1.0	10.7	2.2	6.4	1.0
Galactose	4.4	0.9	7.9	6.4	5.3	1.3	9.2	2.8	9.0	1.2	7.0	1.5
Glucose	19.6	17.3	33.7	29.5	20.6	18.0	47.3	42.2	47.6	51.2	35.3	17.2
Uronic acids	4.7	4.6	3.6	4.2	4.1	3.6	3.6	3.0	3.5	2.8	3.1	4.0

[a] Fractions H_{1a}, H_{2a}, H_{3a}, H_{4a}, H_{5a}, and H_{6a} represent the hemicellulosic polymer preparations degraded during the steam explosion pre-treatments in samples 1, 2, 3, 4, 5, and 6 in Table 1, respectively, while the fractions H_{1b}, H_{2b}, H_{3b}, H_{4b}, H_{5b}, and H_{6b} represent the hemicellulosic preparations released during the alkaline peroxide post-treatments of the corresponding steam exploded wheat straw samples.

hydrolysis and degradation, even though other factors may have also influenced the overall mass balance including partial degradation of more accessible regions of cellulose and lignin. Table 2 gives the content of neutral sugars (relative% hemicellulosic sample, w/w) and uronic acids (% hemicellulosic sample, w/w) in the two groups of degraded hemicellulosic polymers. Clearly, the pre-treatment time and temperature had major influence on the sugar composition of the hemicelluloses degraded during both steam pre-treatment and alkaline peroxide post-treatment. Xylose was the dominant sugar component in the four survived hemicellulosic polymer preparations H_{1a}, H_{1b}, H_{3a}, and H_{3b}, degraded during the steam pre-treatment at 200 °C/15 bar for 10 min and 220 °C/22 bar for 3 min, and released during the corresponding alkaline peroxide post-treatment, comprising 64.7–76.3% of the total sugars. This higher content of xylose in H_{1b} (76.3%) and H_{3b} (70.3%) than in H_{1a} (69.2%) and H_{3a} (64.7%) indicated that the post-treatment with alkaline peroxide under the condition used mainly cleaved the side chains of xylan. Glucose (17.3–20.6%) appeared in a small amount, and arabinose (4.0–9.2%), galactose (0.9–5.3%), uronic acids (3.6–4.7%), mainly 4-*O*-methyl-glucuronic acid, and mannose (0.7–3.6%) presented in relatively minor quantities. These data implied that the four hemicellulosic polymer fractions comprised a xylan as a major constituent, and the treatments under the conditions given did not resulted in significant breakdown the backbone of the hemicelluloses.

On the other hand, as the steam pre-treatment was performed at higher temperature or a longer time, the content of xylose decreased, while the glucose increased in all the survived hemicellulosic polymer fractions. As shown in Table 2, an increasing in 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 resulted in a decreasing xylose from 69.2 (H_{1a}) to 39.9% (H_{2a}), from 76.3 (H_{1b}) to 54.2% (H_{2b}), from 64.7 (H_{3a}) to 28.6 (H_{4a}) and to 26.2% (H_{5a}) and from 70.3 (H_{3b}) to 47.8 (H_{4b}) and to 39.9% (H_{5b}), and an increasing glucose from 19.6 (H_{1a}) to 33.7% (H_{2a}), from 17.3 (H_{1b}) to 29.5% (H_{2b}), from 20.6 (H_{3a}) to 47.3 (H_{4a}) and to 47.6% (H_{5a}), and from 18.0 (H_{3b}) to 42.2 (H_{4b}) and to 51.2% (H_{5b}), respectively. This decreasing trend of xylose content and increasing trend of glucose content as the increasing pre-treatment period revealed that cellulose was continuously degraded into small molecules and co-recovered with the survived hemicellulosic polymers at a longer pre-treatment period. This is probably that an increase in substrate pore volume occurs as a result of hemicellulose hydrolysis, causing a substantial increase in the degradation of cellulose. Similarly, the 4-*O*-methyl-glucuronic acid substituents were also more labile with increase steaming time and temperature as shown by a decrease of uronic acids with an increment in pre-treatment time and temperature. The results obtained were consistent with the findings from xylo-oligosaccharides from steamed birchwood by Korte et al. (1991). They stated that in the steaming extract of 170 °C every 14th xylose unit remained substituted by a 4-*O*-methyl-glucuronic acid side groups (0.07 substituents per xylose unit). At 190 °C every 38th xylose units was substituted by a 4-*O*-methyl-glucuronic acid residue, whereas only every 90th xylose unit was substituted, when birchwood was processed at 210 °C. Surprisingly, increasing water to straw ratio from 2:1 to 10:1 during the steam pre-treatment at 220 °C/22 bar for 5 min did not led to substantial degradation of cellulose as shown by their increases of xylose from 28.6 (H_{4a}) and 47.8 (H_{4b}) to 47.5 (H_{6a}) and 69.3% (H_{6b}), and decreases of glucose from 47.3 (H_{4a}) and 42.2 (H_{4b}) to 35.3 (H_{6a}) and 17.2% (H_{6b}), respectively.

Also, a substantial portion of the water-soluble material (mono- or oligo-saccharides) produced during the steam pre-treatment (20.5–28.5% of the dry straw) was not identified. It was only quantified by differences between the total hemicelluloses and the recovered hemicellulosic and lignin polymers as well as the residual hemicelluloses in the pre-treated residues. This may be explained by the high percentage of chemical transformation and by the condensation reactions between carbohydrates, their degradation products and phenols derived from lignin degradation (Bolanos et al., 2001). However, it should be noted that over half of the hemicelluloses were significantly hydrolysed into mono- or oligo-saccharides, and some of them further produced furfural derivatives such as furfural from xylosyl residues and 5-hydroxymethylfurfural from

Table 3
The content of lignin (% hemicellulosic sample, w/w) in isolated hemicellulosic polymer fractions and its composition of phenolic acids and aldehydes obtained by alkaline nitrobenzene oxidation

Phenolic acids and aldehydes	Hemicellulosic fractions[a]											
	H_{1a}	H_{1b}	H_{2a}	H_{2b}	H_{3a}	H_{3b}	H_{4a}	H_{4b}	H_{5a}	H_{5b}	H_{6a}	H_{6b}
p-Hydroxybenzoic acid	0.11	0.041	0.081	0.41	0.20	0.10	0.15	0.06	0.10	0.05	0.11	0.06
p-Hydroxybenzaldehyde	0.075	0.043	0.067	0.032	0.11	0.08	0.096	0.07	0.087	0.05	0.066	0.05
Vanillic acid	0.11	0.045	0.10	0.031	0.11	0.08	0.13	0.06	0.12	0.06	0.054	0.07
Vanillin	0.45	0..37	0.35	0.17	0.64	0.32	0.56	0.30	0.48	0.29	0.39	0.29
Syringic acid	0.03	0.008	0.02	0.010	0.05	0.01	0.04	0.01	0.02	0.03	0.03	0.04
Syringaldehyde	0.29	0.26	0.26	0.14	0.32	0.16	0.33	0.21	0.32	0.24	0.30	0.21
Acetovanillin	0.09	0.07	0.07	0.06	0.16	0.10	0.18	0.12	0.11	0.14	0.07	0.09
Acetosyringone	0.10	0.015	0.05	0.06	0.08	0.011	0.12	0.08	0.13	0.08	0.05	0.06
p-Coumaric acid	0.003	0.022	0.002	0.011	0.03	0.03	T[b]	T	ND[c]	ND	T	0.02
Ferulic acid	0.006	0.016	0.005	0.011	0.04	0.02	T	T	ND	ND	T	0.03
Cinnamic acid	0.02	0.018	0.016	0.03	0.03	0.03	0.05	0.03	0.03	0.02	0.03	0.02
Total	1.28	0.91	1.05	0.99	1.77	0.94	1.66	0.94	1.40	0.96	1.10	0.94
Content of klason lignin	3.81	2.40	3.12	2.49	4.63	2.16	4.41	2.24	4.02	2.32	3.33	2.27

[a] Corresponding to the hemicellulosic polymer fractions in Table 2.
[b] T, trace.
[c] ND, not detected.

glucosyl residues during steam explosion by the acetic acid (Suzuki et al., 1998).

3.3. Content of lignin

Results concerning the characterization of lignin associated in degraded hemicellulosic polymer preparations are listed in Table 3. The data showed that the twelve hemicellulosic polymers contained relatively low amounts of bound lignins, ranging between 2.2 and 4.6%. This low content of linked lignin in hemicelluloses indicated that steam pre-treatment at elevated temperature and lower in acidity is more dramatic in terms of cleavage of lignin-carbohydrate bonds than mild acidolysis due to the higher temperature involved (Sun & Tomkinson, 2000). This cleavage is particularly true in a longer pre-treatment duration, since an increase in pre-treatment time from 10 to 33 min at 200 °C/15 bar resulted a decrease in lignin content from 3.8 (H_{1a}) to 3.1% (H_{2a}). A similar decreasing trend was observed at 220 °C/22 bar as shown by a decreasing lignin content from 4.6 (H_{3a}) to 4.4 (H_{4a}) and to 4.0% (H_{5a}) with an increase in pre-treatment time from 3 to 5 and to 8 min. In addition, It is very likely that the content of bound lignin in six hemicellulosic polymers preparations H_{1a}–H_{6a} degraded during the steam pre-treatment, 3.1–4.6%, was higher than that of the corresponding six hemicellulosic fractions H_{1b}–H_{6b} released during the alkaline peroxide post-treatment, 2.2–2.5%. This, in one hand, demonstrated that the α-benzyl ether linkages between lignin and hemicelluloses were significantly cleaved during the post-treatment under the condition given. On the other hand, this observation showed that more condensation and repolymerization reactions between the degradation products of hemicelluloses and lignin took place during the steam pre-treatment so resulting in increased klason lignin in H_{1a}–H_{6a}. This coincided with the findings by Chua and Wayman (1979), who declared that under dramatic conditions of steam pre-treatment, the reactive hemicellulose degradation products, such as furfural and its precursors, can react with lignin during autohydrolysis. During steam explosion two types of reactions occur: initially a faster reaction, depolymerization of native lignin and hemicelluloses by acidic hydrolysis, and, as heating continues, condensation and repolymerization reactions take over, thus resulting in increasing the acid insoluble residue, klason lignin (Nergro et al., 2003). The major products, obtained from the alkaline nitrobenzene oxidation of the bound lignin in hemicelluloses, were identified to be vanillin and syringaldehyde, indicating that the associated lignin in the hemicelluloses was composed mainly of non-condensed guaiacyl and syringyl units. A noticeable amount of vanillic acid, *p*-hydroxybenzoic acid, and *p*-hydroxybenzaldehyde and minor quantities of syringic acid, acetovanillin, and acetosyringone as well as traces of *p*-coumaric acid, ferulic acid, and cinnamic acid were also detected in the nitrobenzene oxidation mixtures.

3.4. Weight-average molecular weight

In this study the molecular weights of degraded hemicellulosic polymers were analysed by GPC. From the GPC chromatograms, the weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) were calculated and the data are given in Table 4. Obviously, due to the mild acid hydrolysis at high temperature during the steam pre-treatments, the twelve survived hemicellulosic fractions showed a much lower degree of polymerisation (DP, 82–123), with molecular-average weights ranging from 12,120 to 18,210 g mol^{-1}, indicating that the hemicellulosic

Table 4
Weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) of the hemicellulosic polymer preparations

	Hemicellulosic fractions[a]											
	H_{1a}	H_{1b}	H_{2a}	H_{2b}	H_{3a}	H_{3b}	H_{4a}	H_{4b}	H_{5a}	H_{5b}	H_{6a}	H_{6b}
M_w	14,290	15,810	12,120	14,130	15,930	15,430	14,830	16,710	13,860	16,540	14,020	18,210
M_n	4760	5450	3790	5040	5730	6010	5120	5220	4620	5010	5190	7000
M_w/M_n	3.0	2.9	3.2	2.8	2.8	2.9	2.9	3.2	3.0	3.3	2.7	2.6

[a] Corresponding to the hemicellulosic polymer fractions in Table 2.

polymers were heavily degraded under the steam conditions used. This reduction in chain length of the hemicelluloses resulted partially also from the action of heat and pressure produced during the steam pre-treatments. An increase of steam pre-treatment time from 10 to 33 min at 200 °C/15 bar or at 220 °C/22 bar increasing steam incubation period from 3 to 8 min led to a decrease of degraded hemicellulose molecular weights by 15.2% from H_{1a} to H_{2a} and by 13.0% between H_{3a} and H_{5a}. There were no significant differences in molecular weights between the hemicellulosic polymer fractions H_{1b}–H_{6b} released during the alkaline peroxide post-treatment as shown by their M_w ranging between 15,430 and 18,210 g mol^{-1}.

3.5. FT-IR spectra

The effect of steam pre-treatment conditions on the structure of the hemicelluloses was also demonstrated by FT-IR in the region of 400–4000 cm^{-1}. Fig. 2 illustrates FT-IR spectra of hemicellulosic preparations H_{2a} (spectrum 1), H_{3a} (spectrum 2), and H_{5a} (spectrum 3) degraded during in the steam explosion pre-treatments. Surprisingly, all the three spectra had a specific band maximum in the 1200–1000 cm^{-1}, which are typical of xylans. This region is dominated by ring vibrations overlapped with stretching vibrations of (C–OH) side groups and the (C–O–C) glycosidic bond vibration. In particular, the band between 1118 and 1030 cm^{-1} is dominated by glycosidic linkages ν (C–O–C) contribution (Kacuraková, Belton, Wilson, Hirsch, & Ebringerová, 1998). In the carbonyl stretching region, a strong band at 1628 cm^{-1} is assigned to the absorbed water. A shoulder at 1739 cm^{-1} in the spectrum 2 of hemicellulosic fraction H_{3a} degraded during the steam pre-treatment at 220 °C/22 bar for 3 min is attributed to the acetyl and uronic ester groups of the hemicelluloses or from the ester linkage of carboxylic group of the ferulic acid, whereas the absence of this signal in the spectra 1 and 3 indicated that the steam pre-treatments at 200 °C/15 bar for 33 min or at 220 °C/22 bar for 8 min completely cleaved this ester bond from the hemicelluloses. The small band at 903 cm^{-1}, which represents the C-1 group frequency or ring frequency, is characteristic of β-glycosidic linkages between the sugar units (Geng, Sun, Sun, & Lu, 2003). The bands at 1434,1374, and 1328 cm^{-1} arise from C–H, OH or CH_2 bendings. The occurrence of a very small band at 1520 cm^{-1} in all the spectra is due to the presence of small amounts of associated lignin in the degraded hemicelluloses, which corresponded to the results obtained by alkaline nitrobenzene oxidation.

The FT-IR spectra of hemicellulosic preparations H_{2b}, H_{3b}, and H_{5b} solubilized during the alkaline peroxide post-treatment of the corresponding steam exploded wheat straw are shown in Fig. 3 spectra 1, 2, and 3, respectively. The most obvious feature of these similar spectra is more typical of arabinoxylans, indicating that the alkaline peroxide post-treatment under the condition given did not result in significant changes in the structure of hemicelluloses. The absorbances at 1381, 1328, 1168, 1069, and 903 cm^{-1} in the spectra are associated with hemicelluloses. The lignin-related absorbance at 1513 cm^{-1} is rather weak, indicating minor quantities of the associated lignin. This is in agreement with the content of bound lignin in the hemicelluloses.

3.6. ^1H and ^{13}C NMR spectra

Fig. 4 shows ^{1}H-NMR spectrum of the hemicellulosic fraction H_{3a} degraded during the steam pre-treatment at 220 °C/22 bar for 3 min. The chemical shifts of 3.2–4.4 ppm arise from the equatorial proton and other protons of anhydroxylose units of hemicelluloses. The methyl protons of few amounts of acetyl group and 4-*O*-methyl-D-glucuronic acid exhibit weak peaks at 1.8 and 1.1 ppm, respectively. Anomeric protons of terminal α-D-arabinofuranosyl residues give a shoulder at 5.2 ppm (Teleman, Lundqvist, Tjerneld, Stalbrand, & Dahlman, 2000).

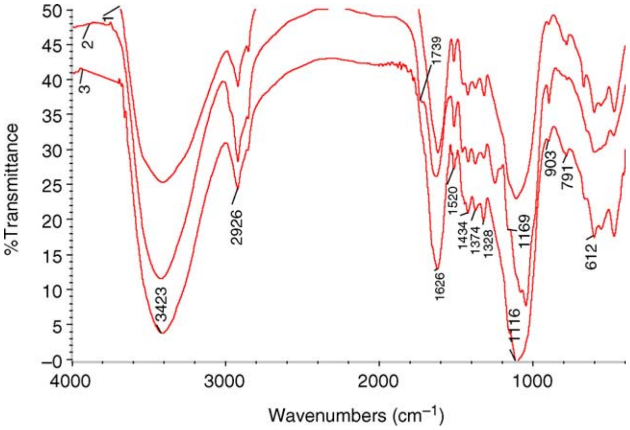

Fig. 2. FT-IR spectra of hemicellulosic preparations H_{2a} (spectrum 1), H_{3a} (spectrum 2), and H_{5a} (spectrum 3) degraded during in the steam explosion pre-treatments.

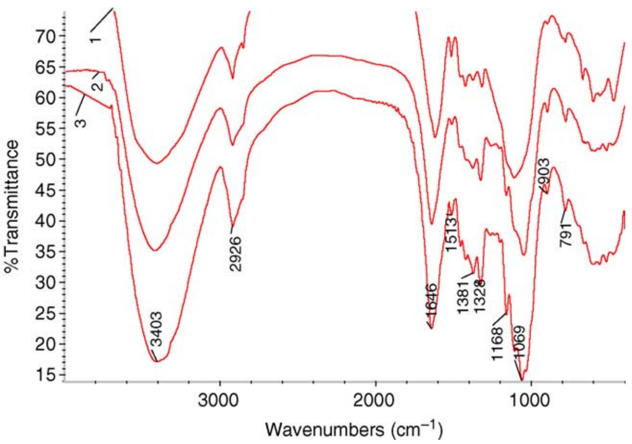

Fig. 3. FT-IR spectra of hemicellulosic preparations H_{2b} (spectrum 1), H_{3b} (spectrum 2), and H_{5b} (spectrum 3) solubilized during the alkaline peroxide post-treatment of the corresponding steam exploded wheat straw samples.

A strong signal at 4.7 ppm is originated from the residual solvent (HDO).

The structures of the hemicellulosic fractions H_{3a} and H_{2b} were also revealed by ^{13}C NMR spectroscopy (Fig. 5). Most of the major resonances were assigned by references to data in literature (Gabrielli, Gatenholm, Glasser, Jain, & Kenne, 2000; Imamura, Watanabe, Kuwahara, & Koshijima, 1994; Sun et al., 1996). The main 1,4-linked β-D-Xyl*p* units are obviously characterized by five strong signals at 102.2 or 102.0, 75.8 or 75.9, 74.8 or 74.9, 73.1 or 73.3, and 63.2 or 63.3 ppm, which are assigned respectively to C-1, C-4, C-3, C-2, and C-5 positions of the β-D-Xyl*p* units. Two intensive signals at 172.0 (spectrum b) and 57.3 (spectrum a) or 56.0 ppm (spectrum b) together with a weak peak at 69.5 ppm (spectrum a) are indicative of C-6, 4-*O*-methoxyl group and C-5 of glucuronic acid residue in the xylan, respectively. Two signals at 78.1 and 61.2 ppm relate to C-4 and C-6 of the glucose residue in the xylan or degraded fragments of cellulose. Acetyl CH_3 in xylan gives a small signal at 23.3 ppm. The presence of minimal quantities of associated lignin was identified by two weak signals at 181.4 and 180.1 ppm, which originates from the carbonyl group in associated lignin.

3.7. 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 hemicelluloses. The thermal degradability is affected by the chemical composition of the material because different components of lignocellulosic materials have different thermal behaviours. Fig. 6 shows typical TGA/DSC curves of hemicellulosic fractions H_{3a} and H_{3b} obtained from wheat straw subjected to steam pretreatment at 220 °C/22 bar for 3 min and the sequential

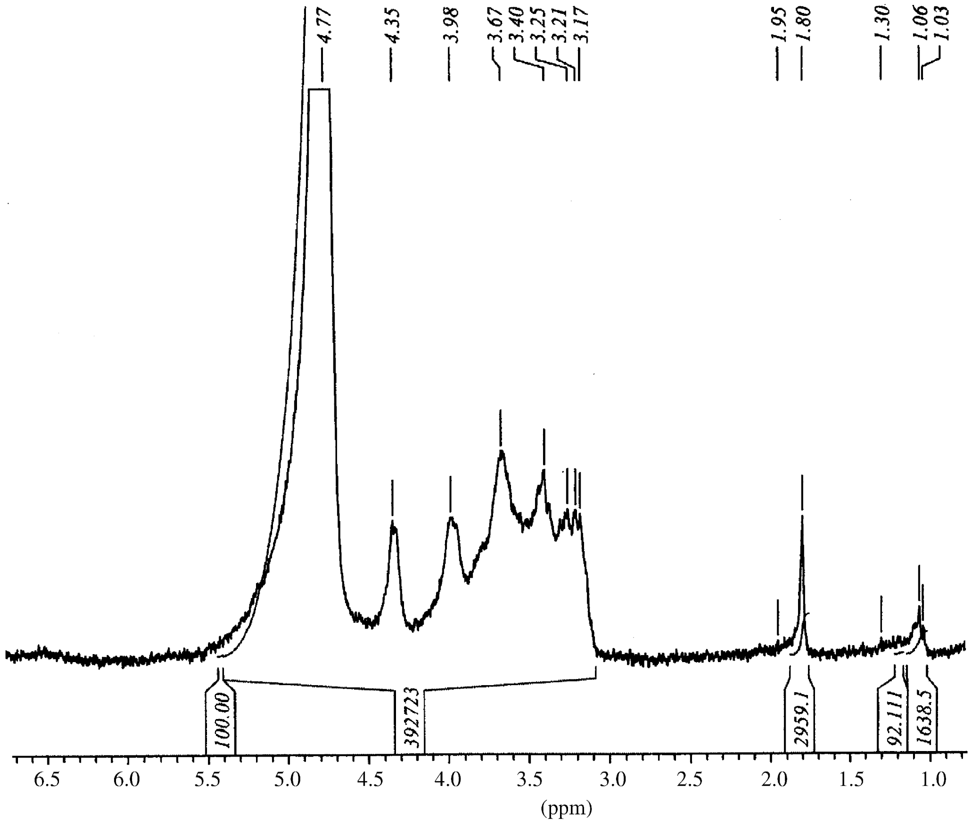

Fig. 4. ^1H-NMR spectrum of the degraded hemicellulosic polymer fraction H_{3a}.

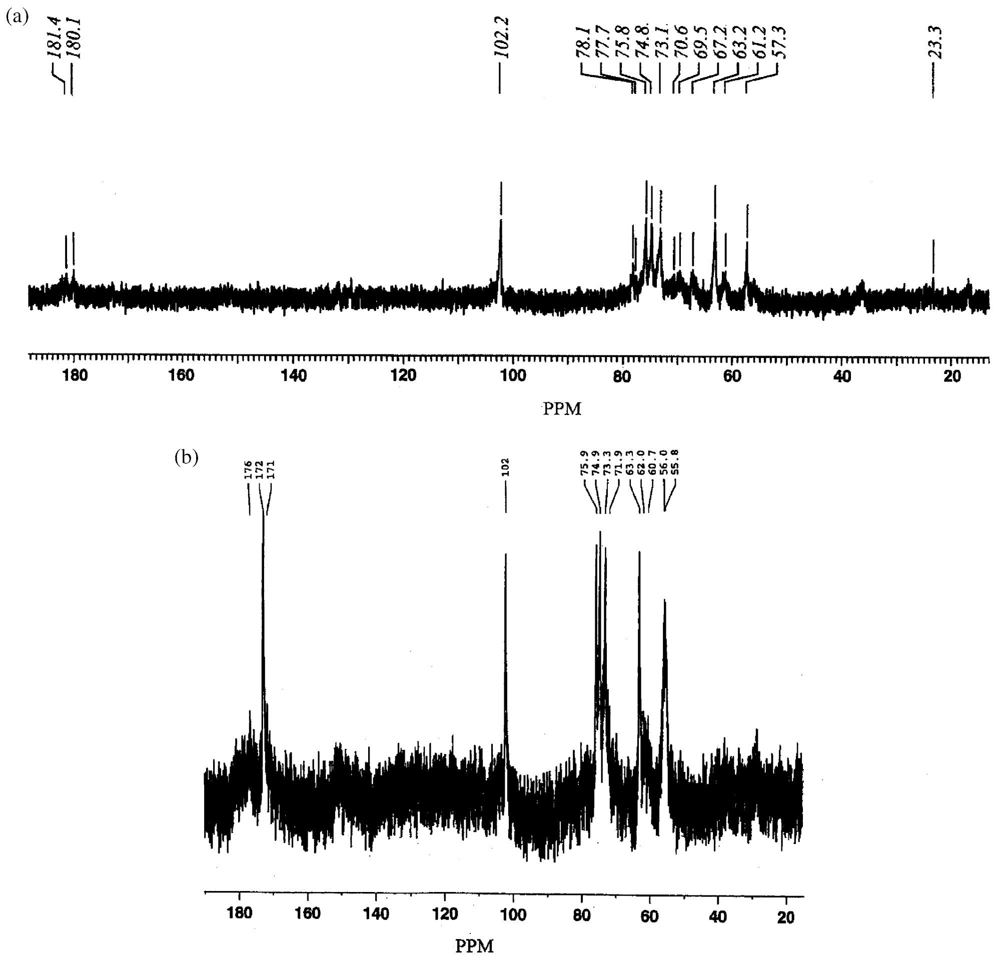

Fig. 5. ^{13}C-NMR spectra of hemicellulosic polymer fractions H_{3a} (spectrum a) and H_{2b} (spectrum b).

alkaline peroxide post-treatment. From the analysis of thermogravimetric curves it can be observed that decomposition of the two hemicellulosic polymer fractions H_{3a} and H_{3b} takes place at 248 and 215 °C, respectively. Similarly, when weight loss arrived at 50%, the temperature raised to 415 and 362 °C for hemicellulosic preparations H_{3a} and H_{3b}, respectively. This phenomenon implied that the hemicellulosic fraction H_{3a} degraded during the steam pre-treatment, had a higher thermal stability than that of the hemicellulosic preparation H_{3b} released during the alkaline peroxide post-treatment. The reason for this higher thermal stability of the hemicellulosic polymers degraded during the steam pre-treatment, was probably due to the generation of condensation substances between the hemicellulose degradation products, leading to a more recalcitrant residue that requires higher temperature ranges for complete decomposition. This was also confirmed by their high residues of 40% for H_{3a} and 34.2% for H_{3b} at 600 °C. In addition, as can be seen from Fig. 6, the H_{3a}, obtained from steam pre-treatment of wheat straw at 220 °C/22 bar had an exothermic peak centred at 311 °C, however, H_{3b}, obtained by the sequential alkaline peroxide post-treatment showed two exothermic peaks centred at 237 and 332 °C, respectively.

4. Conclusions

Briefly, processing of wheat straw by steam explosion pre-treatment and sequential alkaline peroxide post-treatment allows the fractionation of the three main polymers present in the lignocellulosic matrix with reasonable yields and purity, and appears to be a promising technique for practical application of this by-product. The yields of

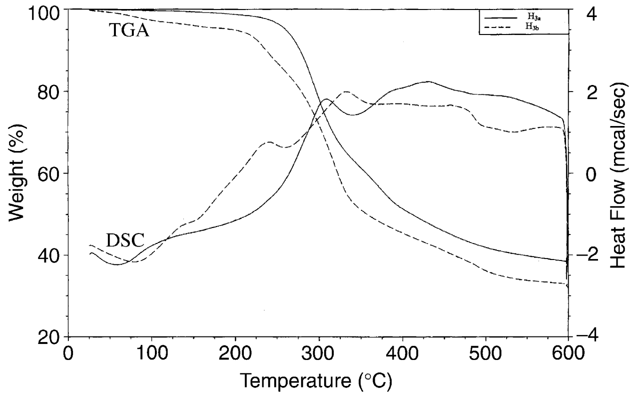

Fig. 6. TGA/DSC curves of hemicellulosic polymer fractions H_{3a} and H_{3b}.

cellulose, lignin, and hemicelluloses are strongly dependent on the steam pre-treatment conditions such as temperature, incubation time, and water to straw ratio. From the assessment of the results it can be inferred that the steam pre-treatment under the conditions used is significantly related to the changes occurred in hemicellulosic polymers. The oligomers and monomers obtained by hydrolysis of the hemicelluloses during the steam pre-treatment accounted for 20.5–28.5% of the dry starting straw, and their yields continuously increased as the pre-treatment temperature and time increase. Small fraction of degraded hemicellulosic polymers (2.4–6.2% of the dry straw) was recovered by precipitation in ethanol, which was composed mainly of xylan together with noticeable amounts of cellulose degradation products and had an average chain length between 82 and 108. These hemicellulose degradation products were also condensed to form more thermostable substrates. Alkaline peroxide post-treatment under the condition given resulted in a release of 23.8–34.6% of the total original hemicelluloses, which had a degree of polymerisation (DP) ranging between 95 and 123, with molecular-average weights from 14,130 to 18,210 g mol^{-1}, and were relatively free of bound lignin (2.2–2.5% klason lignin). These oligomers and monomers hydrolysed from the hemicelluloses as well as the degraded hemicellulosic polymers could be used as a variety of chemicals for industry. However, further studies and large-scale experimentation will be necessary in order to evaluate the economic suitability of the whole process.

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