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Development of a method for the production of hemicellulosic gels from Sitka spruce

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Abstract

Timber can be used as a sustainable source for process chemicals (Silvichemicals), with particular emphasis being placed on wood as source of chemical feedstocks. Bulk Silvichemicals are unlikely to be cost competitive with fossil fuel derived chemicals at present so ideally, research should be directed towards materials with exploitable properties and high intrinsic value in the market place. Research has generally been aimed at the utilisation of cellulose, extractives or degradation products with only minor interest in the utilisation of undegraded hemicelluloses. To increase the intrinsic value the environmental credentials of the product must be considered. The aim of this study was to development a mechanical and/or mild chemical method for the extraction of hemicelluloses in the form of gels. A number of parameters were tested and are detailed and discussed in terms of effectiveness and feasibility. Mechanical refining followed by mild alkaline extraction was found to be effective on a laboratory scale.

Keywords: Hemicellulose; Extraction; Timber; Renewable feedstock

1. Introduction

Renewable resources are increasingly being seen as an important source of new products and materials, particularly with the realization that fossil fuel sources are finite within the foreseeable future. Plants present a large source of natural polymers and there is great potential for the use of non-food crops and crop waste as a renewable resource. Timber can also be used as source of chemicals and chemical feedstocks (termed Silvichemicals) with the three main cell wall components – cellulose, hemicellulose and lignin – being the main potentially exploitable polymers. The main focus of research into this area to date has been to use the cellulose (Galbe, Liden, & Zacchi, 2005; Robinson, Keating, Mansfield, & Saddler, 2003), any extractives or degradation products such as monosaccharides (Ramsay, Hassan, & Ramsay, 1998; Robinson et al., 2003) pyrolysis products (Demirbas & Balat, 2006; Mohan, Pittman, & Steele, 2006), and technical lignin (El Mansouri & Salvad, 2006), with only little interest in undegraded hemicellulose. Hemicelluloses constitute 20–30% of the bulk of annual and perennial plants and timber and are thus among the most abundant of natural polymers (Lindblad, Albertsson, Ranucci, Laus, & Giani, 2005). However, given current economic realities, Silvichemicals will not be competitive with fossil fuel derived chemicals in the same market. To be economically viable they must exhibit exploitable properties which have intrinsic value in their own right.

Several authors have reported methods of isolating hemicellulose (Jacobs, Lundqvist, Stålbrand, Tjerneld, & Dahlman, 2002; Lundqvist et al., 2003; Stålbrand et al., 2004; Willfor & Holmbolm, 2004; Willfor, Sundberg, Hemming, & Holmbom, 2005) from timber and some methods of modifying hemicelluloses e.g. hydrogel formation

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(Lindblad et al., 2005) have been described. The main impediment to extraction of the hemicellulose is the presence of lignin, with the most commonly used method for its removal being chemical delignification (pulping plus bleaching) which requires considerable capital expenditure and may have serious environmental effects because of the effluents.

When contemplating isolation methods from timber environmental issues should also be taken into account. Forest biomass can be used as a sink for anthropogenic carbon dioxide (Booth & Elliot, 1993) but as the trees reach maturity they need to be harvested (and the area replanted) to ensure continued sequestration. If this timber is to be used as a source of Silvichemicals then any procedures must strive to be carbon neutral and have a low environmental impact. Chemicals with a high environmental impact should ideally be avoided and energy requirements kept as low as possible or met by co-generation.

The current research has focused on one species of softwood timber, namely Sitka spruce (*Picea sitchensis*). A large proportion (49% (Forestry Commission, 2005)) of United Kingdom timber production is Sitka spruce. Unfortunately, Sitka spruce has poor penetration into the construction market because it has low durability and dimensional stability and is difficult to treat with preservatives. The main market for Sitka spruce is in the paper and pulp and the wood based panel industries. The market for use in pulp and paper is, however, in decline and the market in the wood based panel industry shows no sign of increasing even though there has been an 8% increase in panel production. Instead, there has been a large increase in the use of recycled/recovered wood (Forestry Commission, 2005).

This paper reports the isolation of hemicellulose from Sitka spruce using low chemical input methods combined with mechanical techniques.

2. Method

The Sitka spruce was supplied as fibre (Iggesund paperboard) which was further processed into a pulp using an atmospheric refiner (wet process) and by grinding into flour (dry process). The fibre length of the pulp was analysed using a Bauer McNett and Kajaani FS200 fibre length analyser. Average width and length of the fibres was reduced by approximately 50% in the pulp preparation.

Mild alkaline conditions have been shown to be effective at extracting hemicellulose from wheat straw (Fang, Sun, Salisbury, Fowler, & Tomkinson, 1999) and so formed the basis of the extraction procedure. Variables tested were type and concentration of alkali, effect of temperature, addition of borate and the use of hydrogen peroxide as a delignification/purification agent. (Sun, Nao, Sun, & Sun, 2004).

2.1. Extraction variables

- *Alkali type/concentration*: Four alkaline treatments were tested: (a) 10% sodium hydroxide, (b) 24% sodium hydroxide, (c) 10% potassium hydroxide, (d) 24% potassium hydroxide. Extraction procedure was to mix 0.5 g (oven dry basis) of pulp with 30 ml of alkali in a 250 ml flask. The flasks were then placed on a rotary shaker set for 50 rpm and left for 8 h. The mixture was filtered and the residue washed with a further 30 ml of alkali and 30 ml of deionised water.
- *Effect of temperature*: 0.5 g (oven dry basis) of pulp was extracted with 30 ml of potassium hydroxide in a 250 ml flask. Flasks were then placed in a water bath set at (a) 20 °C or (b) 60 °C and left with frequent shaking for 3 h.
- *Effect of addition of borate*: 10% sodium tetraborate was added to the extraction medium (24% potassium hydroxide) with extraction carried out at 60 °C for 3 h.
- *Effect of addition of hydrogen peroxide*: A 2% solution of hydrogen peroxide was added to the potassium hydroxide solution as a delignification step. Extraction was carried out with and without addition of borate at 60 °C, with frequent shaking for 3 h.
- *Effect of substrate*: To fully investigate the selected method, extractions were carried out on different preparations of Sitka spruce. These were shavings/sawdust, the original fibre obtained for the investigation, flour (dry ground to pass a 355 μm mesh) and the pulp preparation. Extraction was to mix 0.5 g (oven dry basis) of substrate with 30 ml of 24% potassium hydroxide containing 10% sodium tetraborate and 2% hydrogen peroxide. The mixtures were heated to 60 °C with frequent agitation for 3 h.

2.2. Isolation of hemicellulose

Following each extraction the mixture was filtered and the residue washed with a further 30 ml of alkali and 30 ml of deionised water. Hemicellulose was precipitated from the filtrate by neutralising the solution with acetic acid and adding ethanol in the ratio of 3:1. The hemicellulose gel was recovered by centrifugation at 3750 rpm for 10 min.

2.3. Analysis

Dry weight of the hemicellulose gels was determined by drying overnight at 50 °C.

Further non-oven dried hemicellulose samples were analysed on the basis of monosaccharide composition. Hemicellulose samples were hydrolysed by adding approximately 50 mg of the undried gel to 0.5 ml of 72% sulphuric acid. Hydrolysis of the gel form was found to give more reproducible results than if the dried form was used. The mixture was heated in a water bath at 30 °C for 1 h and then diluted to 4% sulphuric acid with deionised water. The diluted mixture was then heated at 105 °C for 150 min, before cooling with ice.

Analysis of the hydrolysate for monosaccharides was performed using High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection (HPAEC–PAD) (Pettersen & Schwandt, 1991) The

Table 1
Comparison of alkali type and concentration

	10%		24%	
	Yield (mg/g dry wt substrate)	Purity (% monosaccharide composition)	Yield (mg/g dry wt substrate)	Purity (% monosaccharide composition)
Sodium hydroxide	139 (51)	20.3 (0.61)	460 (12)	13.2 (3.4)
Potassium hydroxide	122 (26)	34.6 (13.1)	257 (61)	28.3 (12.1)

() Standard deviation.

equipment consisted of a Dionex GP50 gradient pump, ED50 electrochemical detector, AS50 autosampler and a Carbopac™ PA1 column. Samples injected into the system were eluted with 0.004 M NaOH (carbonate free and purged with helium) with post-column addition of 0.3 M NaOH at a rate of 1 ml/min. Run time was 45 min, followed by 8 min elution with 0.5 M NaOH to wash the column and then 15 min elution with 0.004 M NaOH to re-equilibrate the column. The analysis was quantified against three separate standard solutions using Chromeleon™ computer software. Monosaccharides quantified were arabinose, galactose, rhamnose, glucose, xylose and mannose. Monosaccharide purity of the hemicellulose preparation was determined as the percentage composition of the quantified monosaccharides based on a weight/weight ratio.

3. Results

The various extraction parameters had varying effects on the yield and purity of the gels produced and these are detailed below.

The alkali concentration had a noticeable effect on the yield of hemicellulose obtained, with increased concentrations giving higher yields but lower purity. However, the purity (in terms of monosaccharide composition) was increased by use of potassium hydroxide rather than sodium hydroxide (see Table 1).

Temperature was also found to increase the yield of gel but again with a decrease in purity, as shown in Table 2.

Addition of borate was shown to have little effect on the yield and purity of the gel (Table 3). However, addition of borate was shown to change the monosaccharide profile of the gel (Fig. 1) by increasing the proportion of mannose within the hemicellulose complex (Fig. 2). This raises the possibility that the characteristics of the gel can be altered by altering the xylan/mannan ratios by varying the borate level in the extraction.

Addition of hydrogen peroxide was shown to increase the purity of the precipitated hemicellulose complex such that although the gel yield was comparatively lower the actual monosaccharide yield was greatly increased compared to methods without hydrogen peroxide (Fig. 3).

Table 2
Effect of temperature on hemicellulose extraction

	Yield (mg/g dry wt substrate)	Purity (% monosaccharide composition)
20 °C	257 (61)	28.3 (12.1)
60 °C	522 (23)	19.7 (3.5)

() Standard deviation.

Table 3
Effect of borate on hemicellulose extraction

	Yield (mg/g dry wt substrate)	Purity (% monosaccharide composition)
With borate	435 (186)	19.74 (2.8)
Without borate	410 (59)	17.16 (3.7)

() Standard deviation.

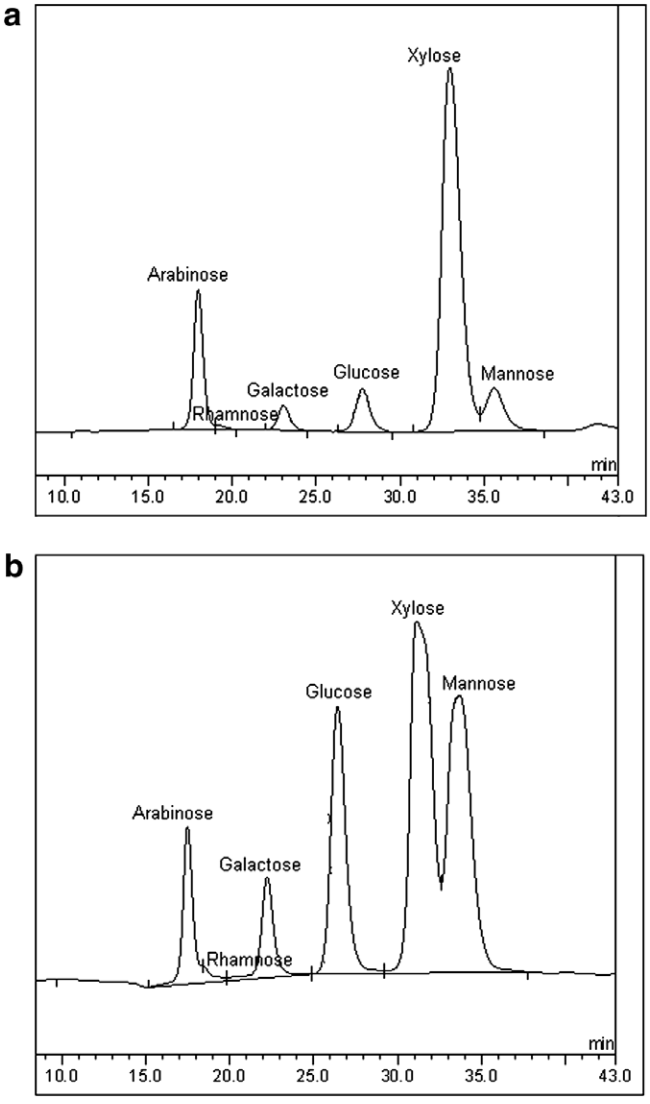

Fig. 1. HPAEC–PAD trace of hemicellulose analysis. (a) Extraction without borate; (b) extraction with borate added.

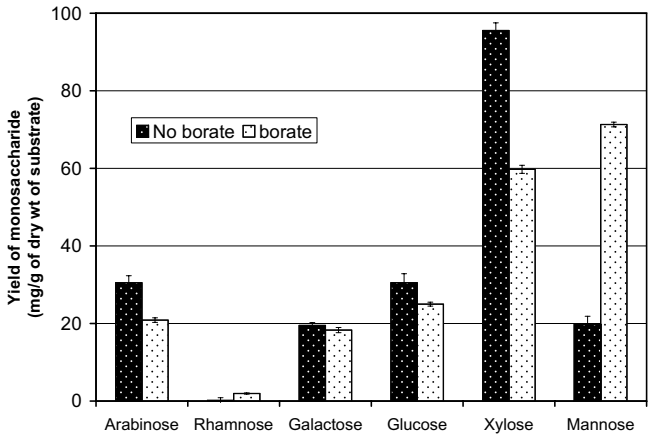

Fig. 2. Effect of borate on monosaccharide composition of hemicellulose extract. (Error bars show standard deviation.)

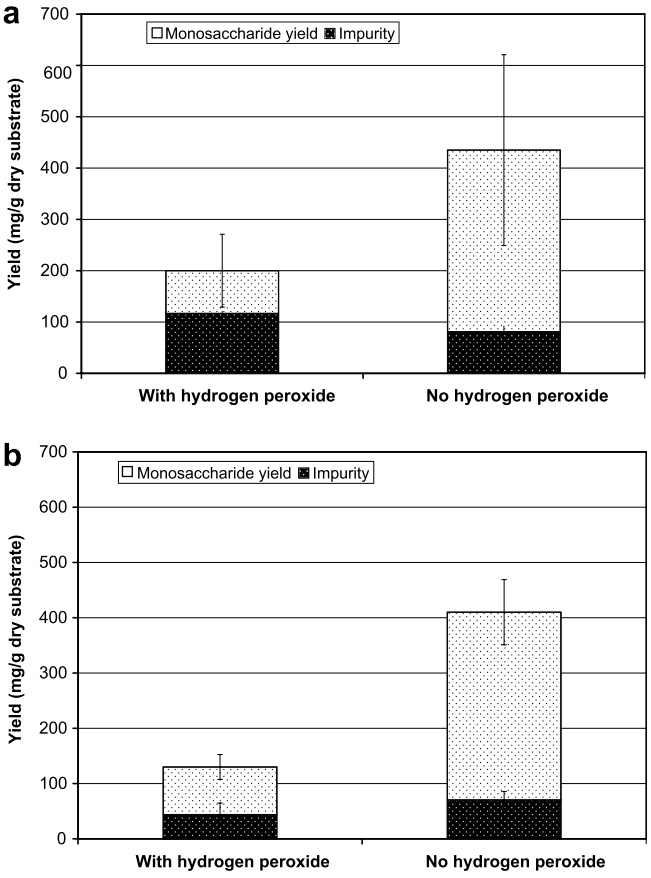

Fig. 3. Effect on hydrogen peroxide on yield and purity of hemicellulose gels (a) with borate and (b) without borate (error bars show standard deviation).

It was found that the yield and the monosaccharide composition also varied depending on the type of substrate used, as shown in Fig. 4. The greatest yield was obtained using flour. It is possible that during pressurized refining to pulp some water-soluble hemicellulosic material was lost. If the process used a closed circulatory system this problem could presumably be avoided. The monosaccharide composition of the hemicellulosic extract

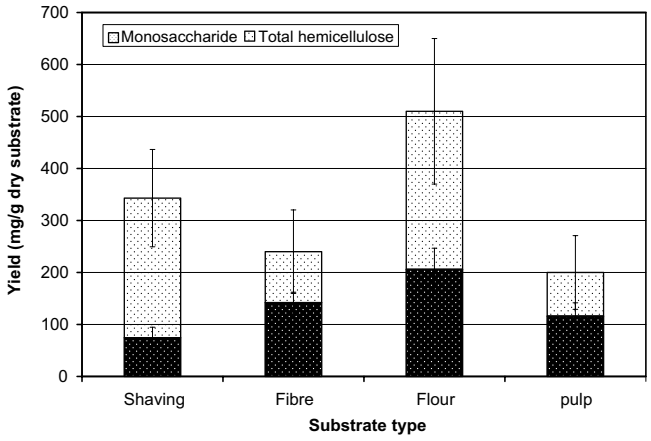

Fig. 4. Effect of substrate type on hemicellulose gels. (Error bars show standard deviation.)

obtained from the flour was higher in arabinose, xylose and mannose than that obtained from the other two substrates.

4. Conclusions

The combination of a mild alkali treatment with addition of hydrogen peroxide at 60 °C was shown to be effective at extracting the hemicellulose from a range of substrates, including timber working residues. This method has the benefit of not using a chlorite bleaching step (for lignin removal), which improves the environmental credentials of the process. Increasing the temperature and alkali concentration was shown to increase yield whilst hydrogen peroxide addition increased the purity (in terms of monosaccharide composition).

It was also shown that it was possible to alter the monosaccharide profile by the addition of borate to the extraction medium. This had the effect of increasing the proportion of mannose within the gels. Although the effect of altering the xylose/mannose ratio on gel properties has not yet been determined it may be possible to adapt or tailor gels to specific end uses simply by varying borate levels in the extraction.

In this study dry ground flour was found to give the highest yields (in terms of monosaccharide composition) using this method. The yield of 206 mg/g dry substrate achieved using dry ground flour compares favourably with the yields obtained from Norway spruce (218 mg/g), White spruce (207 mg/g) and Black spruce (222 mg/g) obtained using harsher techniques (Willfor et al., 2005).

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